**AFML-TR-74-177**
**Part I**
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# STRUCTURE-STABILITY RELATIONSHIPS OF POLYMERS BASED ON THERMOGRAVIMETRIC ANALYSIS DATA

A27

## Part I: Polyaliphatics, Polyalicyclics, Spiro Polymers and Phenylene-R-Polymers

TECHNICAL REPORT AFML—TR—74—177, PART I

DECEMBER 1974



AIR FORCE MATERIALS LABORATORY
AIR FORCE SYSTEMS COMMAND
WRIGHT—PATTERSON AIR FORCE BASE, OHIO 45433

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Dr. Gerhard F. L. Ehlers, Project Scientist

FOR THE COMMANDER:

R. L. Van Deusen, Chief
Polymer Branch
Nonmetallic Materials Division

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13. ABSTRACT

Thermogravimetric analysis data of about 500 aliphatic, alicyclic and aromatic ("phenylene-R-") polymers, and numerous literature data, have been used to correlate polymer structure with thermal stability. The temperature of the extrapolated onset of the first major breakdown step has been used as criterion for thermal stability. The results, by polymer classes, are listed in the discussion section. The maximum stabilities obtained for various polymers and moieties, order of stabilities of linking groups, the effect of lengths of alkylene chains, tacticity, packing, branching, crosslinking, sidegroups and other factors have been discussed.

A second report will deal with aromatic - heterocyclic polymers and summarize the results of both reports.

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| Thermal Analysis | | | | | | |
| Thermogravimetric Analysis | | | | | | |
| Structure | | | | | | |

## FOREWORD

This report covers thermogravimetric analysis data collected between about 1960 and 1973. The sources of the samples, synthesized under Air Force contracts in the majority of the cases are listed at the end of the discussion of each polymer class. Samples with AFML as the source have been synthesized by and obtained from: J. Coleman, G. F. L. Ehlers, R. C. Evers, O. K. Goins, F. L. Hedberg, G. A. Loughran, D. W. Thomson and R. L. Van Deusen. The thermogravimetric analysis determinations have been performed by personnel and students of the University of Dayton Research Institute.

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## SECTION I

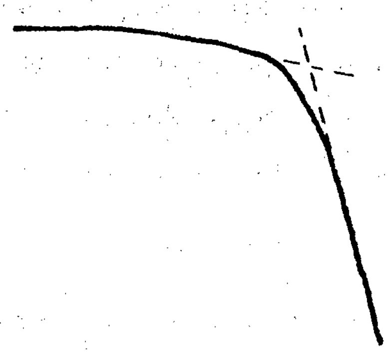
### Discussion

An attempt was made to utilize our extensive file of thermogravimetric analysis (TGA) data on experimental polymers to derive some structure-stability relationships.

TGA data on over 1300 polymers were collected since 1960. The vast majority of these polymers have been synthesized by Air Force contractors or were the result of inhouse work; a few are from other outside sources or commercially available. Of the vast amount of data, those polymers were omitted which, due to the complexity of their structure, were not readily comparable with others. Other results were eliminated if there was doubt about purity and reliability of a given structure.

The TGA data were obtained using a modified Chevenard Thermobalance at a heating rate of about 180°C/hr. Most of the runs were performed in nitrogen, some in air, using a flow rate of 98 cc/min. The sample size in the earliest runs was 200 mg, then 100 mg. After some modifications of the balance had been made to increase sensitivity, a sample size of 50 mg was being used, in porcelain crucibles Coors 0000.

It is well known that a variety of criteria can be used to interpret a TGA curve. Their significances and merits have been discussed frequently in the literature. In this study, the extrapolated onset of the decomposition was used, i.e. the intersection of the tangent of the steepest part of the curve of the first major weight loss step with the tangent of the weight loss curve immediately before the actual (not extrapolated) onset of above weight loss step, as shown below:



Discretion was used to disregard early weight losses which obviously resulted from impurities, water, solvent, etc. The reason for selecting the extrapolated onset of breakdown as criterion is that it signifies the beginning of the first major fragmentation of the polymer under ideal conditions (high molecular weight, no impurities) and, thus, is an indication of the inherent stability of the polymer structure under the conditions used. The extrapolated onset is also close to actual use temperatures of interest and may be correlated to their temperatures easier than events in the higher temperature range. The first breakdown step is also, as work by Grassie and Mc Guchan (Ref. 1) indicated, the most reproducible part of the TGA curve.

The points thus determined are designated Tdec ($N_2$) for runs in nitrogen and Tdec (Air) for runs in air, and listed in degrees centrigrade. If several TGA curves of polymers with the same structure were available, the optimal result normally was used. In the text, the term "stability" refers to Tdec ($N_2$), unless indicated otherwise.*

Literature results were used if they were available as sets of data and could be compared among themselves. Different instrumentation, heating rates and atmosphere normally do not allow comparison with our or other literature data. Again, data which seemed to be questionable for one reason or another were not used. Other results were omitted in cases where the test conditions, especially the atmosphere, were not known. The Tdec's derived from the relatively small TGA curves in literature figures can only be approximate values.

The results are discussed and compared by polymer classes (see Table of Contents). At the end of each class the sources of the investigated polymers are listed, with the exception of those which are covered by the references. The section "Conclusions" finally summarizes the most important findings of general validity, and the comparison between polymer classes.

---

* "Tdec (diff)", where used in this report, designates the difference between the Tdec's of the first and the last of a given group of polymers.

In a subsequent report on heterocyclic polymers, the findings of both reports will be summarized. At that time, attempts will be discussed to correlate these stability data with isothermal conditions.

1. Vinyl Polymers

a. No side-groups or one, non-functional side-group.

| | Tdec ($N_2$) |
|---|---|
| Polyethylene | 415 |
| Polyvinylcarbazole | 415 |
| Polyvinylpyrolidone | 400 |
| Polyvinylcyclohexane | 400 |
| Polybutadiene | 390 |
| Polystyrene | 380 |
| Polyphenylacetylene * | 310 |

The stability of the -C-C- chain is around 400°C. The first two polymers allow closer packing than the rest, which may contribute to their slightly higher stability.

* possibly ill-defined

b. Functional Sidegroups.

$(-CH_2-CHR-)_n$

| R: | Tdec ($N_2$) |
|---|---|
| $-CONH_2$ | 410 |
| $-OC_2H_5$ | 375 |
| -CN | 280 |
| -NCO | 270 |
| -OH | 260 |
| - Cl | 220 |

The significant difference between the major, primary decomposition reactions of the first two and the last four polymers is the fact that the former occur within the side chain only (formation of $H_2O$ and $C_2H_4$, respectively), while the latter involve H-abstraction from the chain, which apparently reduces the stability.

Data by Gilbert and coworkers (Ref. 2) on some of the same polymers agree reasonably well with above data. In addition, the following Tdec's were derived from the TGA curves of above authors:

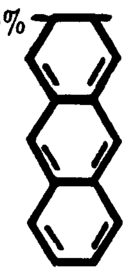
| | Tdec ($N_2$) |
|---|---|
| polyvinyl chloride $(-CH_2-CH\,Cl-)$ | 260 |
| " chlorinated | 220 |
| rubber, chlorinated | 220 |
| polyvinylidene chloride $(-CH_2-C\,Cl_2-)$ | 215 |

Increasing Cl - content may be the reason for the decreasing stability (HCl formation).

c. Double bonds.

Comparison of polyethylene with polybutadiene (see under a) and of polystyrene with polyphenylacetylene (although the latter may not be pure) may suggest that double bonds in the chain decrease stability.

d. Disruption of symmetry and packing.

| | Tdec ($N_2$) |
|---|---|
| Polystyrene | 380 |
| " + 10%  | 305 |

Disruption of symmetry and prevention of close packing decreases stability (see also under Ia).

e. "Head to Tail" vs. "Head to Head".

Murayama and Amagi (Ref. 3) investigated the thermal stability of "head to tail" and "head to head" polyvinylidene chloride and polyvinyl chloride ($\Delta T = 150°C/hr$, Argon). The following Tdec's have been obtained from their curves:

| | | Tdec ($N_2$) |
|---|---|---|
| Polyvinylidene chloride, | H-T | 210 |
| " " | H-H | 320 |
| Polyvinyl chloride, | H-T | 245 |
| " " | H-H | 245 |

The higher stability of the H-H polyvinylidene chloride has been explained by the authors with its higher resistance to unzipping and fewer adjacent hydrogen atoms to one chlorine atom. However, this should also apply to polyvinylchloride. While the two PVC curves are quite different (H-H PVC has a lower actual onset of breakdown, and a lower rate of weight loss), the extrapolated onsets are the same. Authors suggest that the chlorine in H-H PVC is less stable than in H-T PVC, but that the chlorine in the initial breakdown product is more stable:

$$-CH_2-\underset{\displaystyle Cl}{\underset{|}{C}}H-\underset{\displaystyle Cl}{\underset{|}{C}}H-CH_2- \longrightarrow -CH_2-CH=\underset{\displaystyle Cl}{\underset{|}{C}}-CH_2-$$

f. Cis-trans Isomerism.

Strauss and Madorsky (Ref. 4) compared the weight loss of natural rubber and guttapercha at a variety of temperatures over a fixed period of time (30 min, plus 45 min heating-up time). Although the data cannot be compared directly with TGA data, "pseudo-TGA curves" can be plotted and indicate that no marked difference exists between the thus obtained Tdec (vac) of these cis and trans isomers.

g. Crosslinking.

| | Tdec ($N_2$) |
|---|---|
| Polystyrene | 380 |
| Polystyrene - 60% Divinylbenzene | 320 |
| Polydivinylbenzene | 390 |

While dense crosslinking (polydivinylbenzene) results in a slightly improved stability, the copolymer shows decreased stability, possibly because the loose network is less densely packed than the polystyrene itself. Contrary to these findings, however, Madorsky and Strauss (Ref. 5-7) found distinctly increased stability with increasing crosslinking density from "pseudo-TGA" data (weight loss-temperature curves from heating individual samples 30 min. at each temperature):

| | Extrapolated Onset |
|---|---|
| Polystyrene | 345 |
| " + 2% Divinylbenzene | 345 |
| " + 25% Divinylbenzene | 355 |
| " + 48% Divinylbenzene | 388 |
| " + 56% Divinylbenzene | 384 |
| Polystyrene + 25% Trivinylbenzene | 370 |
| Polytrivinylbenzene | 400 |

h. Tertiary and quaternary carbon

Data by Madorsky and Strauss (Ref. 8), using the before-mentioned "pseudo-TGA" approach (45 min exposure at each temperature) gave the following extrapolated onsets for polymers with different contents of tertiary carbon:

| | Extrapolated Onset |
|---|---|
| Polymethylene | 409 |
| Polyethylene | 393 |
| Polypropylene | 373 |

This suggests that tertiary carbons (branching) in the chain decrease the stability.

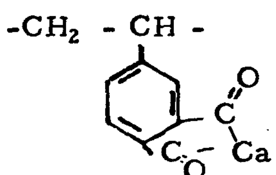
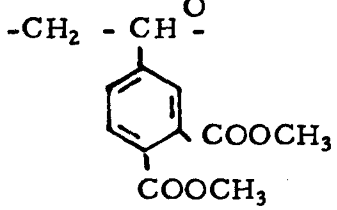
Moving from a tertiary to a quaternary carbon seems to further decrease the stability. McNeill and Neil's (Ref. 9) TGA curves ($\Delta T = 600°C/hr$) yield Tdec's which reflect this difference. The decomposition mechanism of the two polymers is, incidentally, quite different: water is the first and major product of the first polymer, while the second generates predominantly monomer.

| | Tdec ($N_2$) |
|---|---|
| $-CH_2-\overset{H}{\underset{COCH_3}{C}}-$ | 320 |
| $-CH_2-\overset{CH_3}{\underset{COCH_3}{C}}-$ | 305 |

Our own results show identical breakdown temperatures around 330°C for 3 polymers with quaternary carbon atoms independently of their substituents.

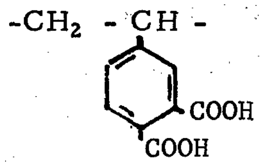
| | Tdec ($N_2$) |
|---|---|
| $-CH_2-\overset{CH_3}{\underset{COOCH_3}{C}}-$ | 335 |
| $-CH_2-\overset{CH_3}{\underset{CHO}{C}}-$ | 330 |
| $-CH_2-\overset{CH_2OH}{\underset{COOC_2H_5}{C}}-$ | 330 |

i. Ring Substitution in Polystyrene.

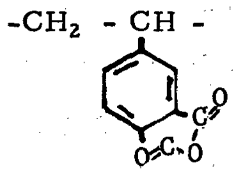
| | Tdec ($N_2$) |
|---|---|
| Polystyrene | 380 |
|  | 470 |
|  | 330 |

The stabilizing effect of the Ca-salt is remarkable. As far as the last three polymers are concerned, the order of stability seems to be related to the ease of decarboxylation and dehydration.

Tdec ($N_2$)

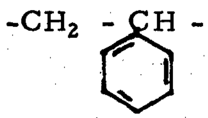


300

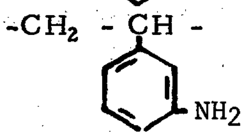


250

Hardly any effect of substitution on Tdec($N_2$) was evident in the TGA curves of poly-m-aminostyrene and poly-m-acetamidostyrene (Still and Keattch, Ref. 10), suggesting that <u>decomposition reactions involving the amino- and acetamido group do not occur before main chain fracture.</u>



390



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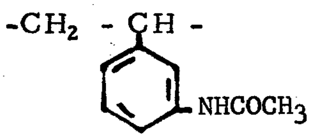


380

k. Air versus Nitrogen.

In those cases where runs in air have been made in our own investigations, the <u>Tdec's (air)</u> were practically <u>identical to the Tdec's ($N_2$)</u>.

Figure 1 shows TGA curves of representative vinyl polymers.

Sources of polymers:

BASF

Chemische Werke Troisdorf

Koppers Co., Inc.

Roehm & Haas

University of Illinois

University of Rhode Island

Unknown origin of several early samples.

2. <u>Fluorovinyl Polymers</u>

a. Polymers not containing hydrogen in the chain; crosslinking.

| | Tdec ($N_2$) | Tdec (air) |
|---|---|---|
| $\left(\begin{array}{l}-CF_2-\underset{\mid}{CF}-\\-CF_2-CF-\end{array}\right)_n$ | 585 | |
| $(-CF_2-CF_2-)_n$ | 540 | 550 |
| $\left.\begin{array}{l}(-CF_2-CF_2-)_n\\ \left(-\underset{CF_3}{\overset{F}{C}}-CF_2-\right)_m\end{array}\right\}$ | 460 | 480 |
| $\left.\begin{array}{l}(-CF_2-CF_2-)_n\\ \left(-\underset{OCF_3}{\overset{F}{C}}-CF_2-\right)_m\end{array}\right\}$ | 450 | 450 |
| $(-CF_2-CFCl-)_n$ | 420 | |
| $(-CF_2-\underset{C_6H_5}{CF}-)_n$ | 315 | 330 |

These polymers fragmentize to form varying amounts of monomers and larger fragments, leaving no residue. Increasing substitution of fluorine by bulkier groups decreases the stability depending upon their frequency and size. Note that Tdec ($N_2$) of poly $\alpha,\beta,\beta$ - trifluorostyrene is below that of polystyrene (380°C).

Crosslinking at every second carbon (see the first two polymers) increases the stability by 45°C.

Jackson (Ref. 11) investigated the decomposition of polyperfluorobut-2-yne ($\Delta T = 600°C/hr$), with the results shown to the left. It is difficult to explain the discrepancies between the run in Argon on one hand and those in vacuum and air on the other.

$$\begin{array}{ccc} CF_3 & & CF_3 \\ \mid & & \mid \\ -C & & C- \\ \parallel & & \parallel \\ C & - & C \\ \mid & & \mid \\ CF_3 & & CF_3 \end{array}$$

Tdec(Argon)
530

Tdec(vac)
620

Tdec(air)
620

b. Polymers containing hydrogen in the chain.

| | Tdec ($N_2$) | Tdec (Air) |
|---|---|---|
| $(-CF_2-CH_2-)_n(-CF_2-\underset{CF_3}{CF}-)_m$ | 440 | |
| $(-CF_2-CH_2-)_n$ | 430 | 430 |
| $(-CF_2-CH_2-)_n(-CFH-\underset{CF_3}{CF}-)_m$ | 420 | 430 |
| $(-CFH-CFH-)_n$ | 365 | |

In addition to the polymers listed above, two copolymers of tetrafluoroethylene and certain nonfluorinated olefins were investigated. These two polymers had Tdec's ($N_2$) of 445 and 465°C. All of these polymers form HF as the first and major decomposition product, and it seems that <u>the ease of HF formation depends upon the proximity between H and F atoms</u>: The closer they are, the easier HF can form, and the lower is the stability.

c. Air versus Nitrogen.

In those cases where Tdec (air) was determined, it was identical to or 10 to 20°C higher than Tdec ($N_2$).

TGA curves of Teflon and Viton A are shown in Figure 2.

Sources of Polymers:

AFML

Dow Corning

Dupont

Koppers Co., Inc.

3-M Company

Monticatini

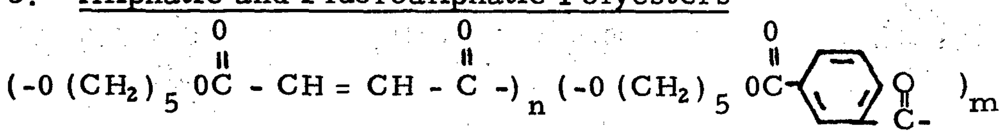
PCR, Inc.

Pennwalt

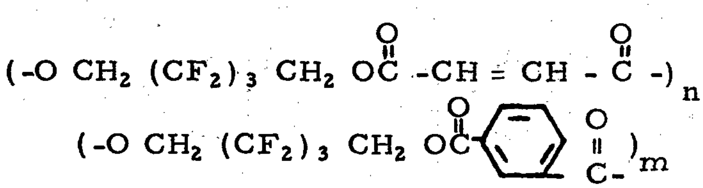
University of Florida

3. <u>Aliphatic and Fluoroaliphatic Polyesters</u>

Tdec ($N_2$)



| | |
|---|---|
| crosslinked with maleimide-triallylcyanurate | 330 |
| crosslinked with triallylcyanurate | 340 |



| | |
|---|---|
| crosslinked with maleimide-triallylcyanurate | 340 |
| crosslinked with triallylcyanurate | 340 |

The results suggest that the Tdec's around 340°C are either connected to the ester linkage or to the cyanurate system, and that the presence of fluoroalkyl moieties has no effect on the stability of these systems.

Source of polymers:

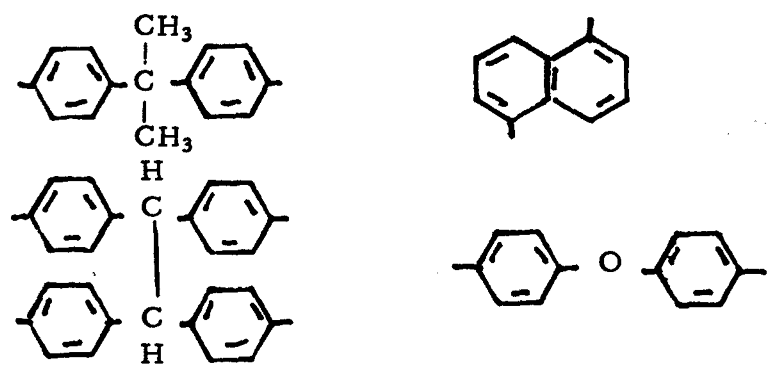
Hooker Chemical Co.

4. Epoxy Resins

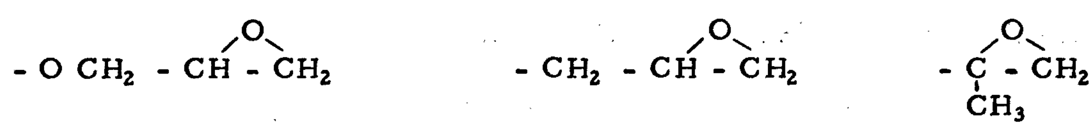
The stability of epoxy resins is affected by the structure of the basic oxirane compound or prepolymer, the curing agent and the curing conditions.

We studied a variety of epoxy resins with the following fluoroalkyl and aromatic moieties:

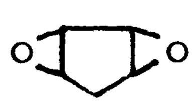
$$-CH_2(CF_2)_nCH_2-$$



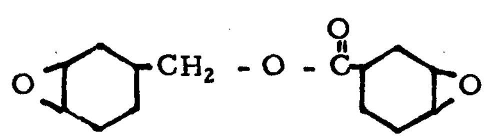
linked to the following oxirane moieties:



and cured with curing agents of the anhydride and amine type, as well as $BF_3$ - monoethylamine. In addition, epoxy resin copolymers on the basis of



and



have been investigated.

In spite of the large variety of systems, Tdec was found to be rather uniformly between about 330 and 390°C. A notable exception was a system cured with chlorendic anhydride, probably forming considerable amounts of hydrogen chloride at relatively low temperatures (Tdec = 260°C). The reason for the uniformity of the results is that all of the cured resins contain an aliphatic ether linkage of the methylene group, and most likely some secondary alcohol groups. Depending upon the epoxy system and the curing agent, they may also contain cycloaliphatic, ester and amine moieties. According to Lee and Neville (Ref. 12), the methylene group and the $-O-CH_2-$ linkage are subject to the initial breakdown reactions. These groups most likely account for the Tdec range of 330 to 390°C. Tdec may be lower in the presence of amino groups (amine cured) and halogen; both groups are, as we found in agreement with above source, detrimental to thermal stability.

Tdec (Air) has been determined only in one case and was identical to Tdec ($N_2$).

A representative TGA curve for a resin of good thermal stability can be seen in Figure 3.

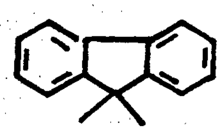
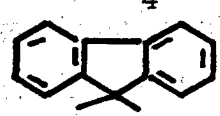
Sources of Polymers:

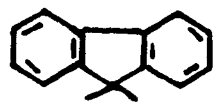
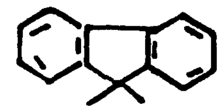
AFML

Shell Chemical Co.

Union Carbide

5. Aliphatic Polyamides

| Diacid Component | Diamine Component | Tdec ($N_2$) |
|---|---|---|
| $-(CH_2)_5NHCO-$ | | 390 |
| $-CO(CH_2)_6CO-$ | $-NH(CH_2)_6NH-$ | 380 |
| $-CO(CH_2)_4CO-$ |  $-NH\,CH_2CH_2CH_2\;\;CH_2CH_2CH_2NH-$ | 390 |
|  $-OC\,CH_2\,CH_2\;\;CH_2\,CH_2\,CO-$ | $-NH(CH_2)_6NH-$ | 380 |

| | | Tdec ($N_2$) |
|---|---|---|
| $-OCCH_2 \cdot CH_2 \quad CH_2 \cdot CH_2CO-$ | $-NHCH_2CH_2 \cdot CH_2 \quad CH_2 \cdot CH_2CH_2NH-$ | 390 |

The uniform Tdec of 380 to 390°C for aliphatic polyamides of quite different structure suggests that the amide linkage is the original site of the chain cleavage reaction.

Figure 4 shows a TGA curve of 6, 6-Nylon.

Sources of Polymers:

Farben fabriken Bayer

Koppers Co., Inc.

Unknown Source

## 6. Polyurethanes

Several commercial and experimental polyurethanes, some with uncertain structure, but all of them with the urethane linkage -NH-CO-O were investigated. The results suggest that Tdec ($N_2$) for the urethane linkeage is between 275 and 310°C.

Sources of Polymers:

Bayer

Unknown Source

## 7. Aliphatic and Alicyclic Polyethers and -imines

| | Tdec ($N_2$) |
|---|---|
| $-CH_2-O-$ | 290 |
| $-\underset{\displaystyle CF_3}{CH}-O-$ | 200 |
| $-\underset{\displaystyle C_3F_7}{CH}-O-$ | 235 |
| α - Cellulose | 320 |
| Rayon | 300 |
| Cellulosetriacetate | 300 |

Polyalkylene oxides and cellulose and its derivatives have ether linkages between aliphatic and/or alicyclic moieties. Tdec's($N_2$) around 300°C apparently can be attributed to the aliphatic-alicyclic ether linkages. Substitution of hydrogen in polymethyleneoxide by perfluoroalkyl groups lowers the stability considerably.

| | Tdec ($N_2$) |
|---|---|
| $-CH_2-CH-N(R)-$ | 200 |
| R = $-CH_2CH_2CN$ or similar | |

A <u>polyethylene imine</u> proved to be <u>considerably less stable than polymethylene oxide</u> (see above).

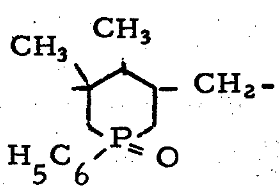
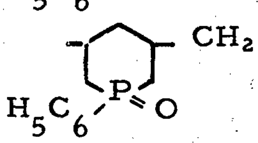
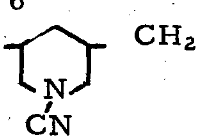
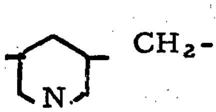
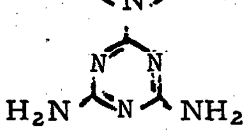
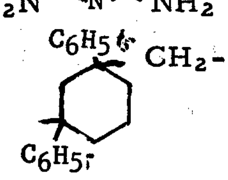
Madorsky and Strauss (Ref. 8) investigated the stability of polyalkylene oxides by the aforementioned "pseudo TGA" approach. The results showed that the unordered, <u>atactic polymer is less stable than the</u> ordered, <u>isotactic polymer</u>.

| | Tdec($N_2$) |
|---|---|
| $-(CH_2)_2O-$ | 330 |
| $-CH_2CH(CH_3)-O-$ (isotactic) | 290 |
| $-CH_2-CH(CH_3)-O-$ (atactic) | 260 |

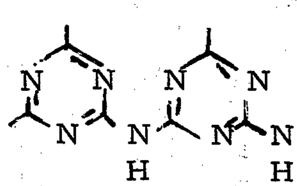
Sources of Polymers:

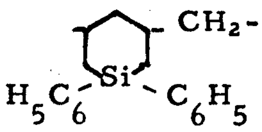
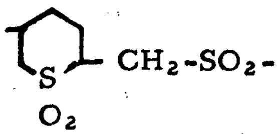
AFML
Bayer
Dupont
Farbwerke Hoechst
Uncertain Sources

8. <u>Alicyclic Polymers from Inter-Intramolecular Polymerization</u>

| | Tdec($N_2$) |
|---|---|
|  | 360 |
|  | 395 |
|  | 410 |
|  | |
|  | 450 |
|  | 350 |

These polymers have in common a <u>non-aromatic ring and a methylene group</u> in the chain, and in general, <u>stabilities between 350 and 410°C</u>. One exception is the polymer with the melamine moiety, which may actually be crosslinked through the amino groups and represent a more stable <u>poly-s-triazinylene imide</u>



| | Tdec($N_2$) |
|---|---|
|  | 410 |
|  | 270 |

with a Tdec($N_2$) of 450°C. Another exception is the polymer at the end of the listing. Its rather low stability is very likely caused by the $SO_2$ groups which are easily removed from this aliphatic-alicyclic system.

Sources of Polymers:

AFML
University of Florida
University of Illinois
University of Iowa

9. Polymers with Bridged Ring Systems

| | Tdec($N_2$) |
|---|---|
| Polynorbornene | 390 |
| Polyhydroxymethylnorbornene | 385 |
| Polycarbomethoxynorbornene | 360 |
| Polynorbornadiene | 370 |
| Polynorbornadiene-butadiene | 390 |
| Polynortricyclene | 400 |

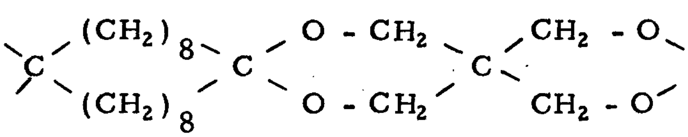
These polymers, in spite of their varieties in structure and pendant groups, have Tdec's within the fairly small range of 360 to 400°C, which possibly may be attributed to the bridged alicyclic system .

Source of Polymers:

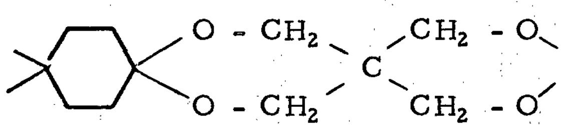
Shell Development Co.
U. S. Rubber

10. Spiro Polymers

The following Tdec's were determined, or derived from literature data as indicated:

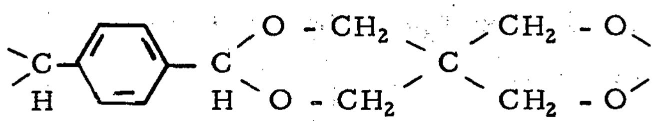


Tdec ($N_2$)
370 ($\Delta T$ = 300°C/hr; ref. 13)

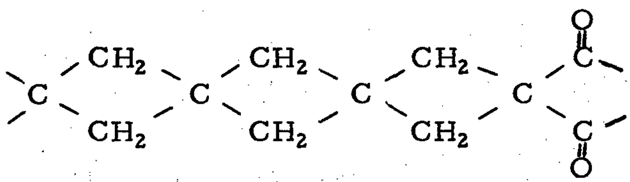
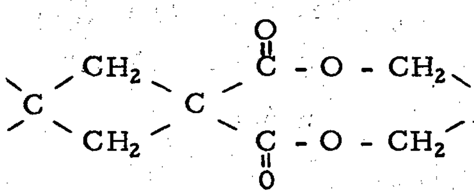


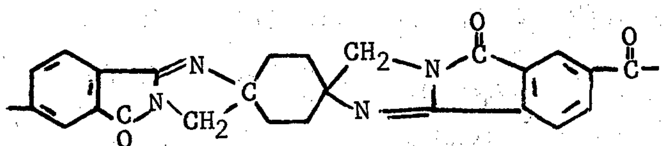
Tdec ($N_2$)

380 ($\Delta T$ = 300°C/hr; ref. 13)



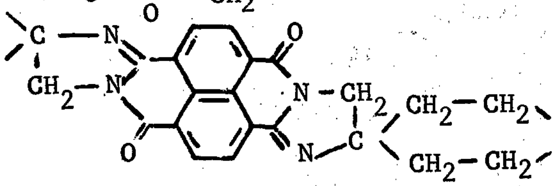
330

| | Tdec ($N_2$) | Tdec (Air) |
|---|---|---|
|  | 365 | 270 |
|  | 350 | 350 |



Tdec (Vac)

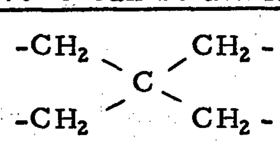
370



510 520

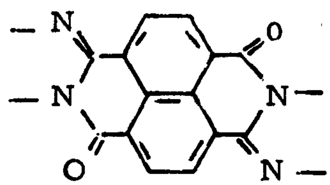
Data on the last two polymers have been derived from results by Heller and coworkers (Ref. 14).

The Tdec's($N_2$) of these spiro polymers are within the small range of 330-370°C, with the exception of the last one. The presence of aliphatic, cycloaliphatic, aromatic or heterocyclic moieties seems to have no effect on the Tdec. It is, therefore, believed that the Tdec ($N_2$, Vac) of 330 to 370°C can be attributed to the spiro linkage common to all these polymers,



(=N′) .

The higher Tdec of the last system may be the result of the stabilizing influence of the very stable, aromatic-heterocyclic ring structure:



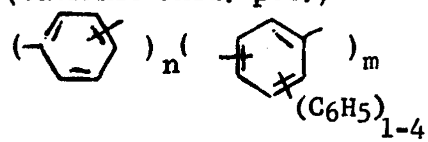
Similar stabilization effects have been, for example, observed in polybenzimidazoles with aliphatic chain moieties.

Sources of Polymers:

Stanford Research Institute

San Diego State University

11. <u>Polyphenylenes</u>

| | Tdec($N_2$) | Tdec (Air) |
|---|---|---|
| Polyphenylene (misc. synth. approaches) | 370-525 | 260-540 |
| " (cationic oxid. polymerization) | 450-660 | |
| " , copolymerized with m-terphenyl, naphthalene, biphenyl (cationic oxid. pol.) | 340-460 | 370-590 |
| Phenylated polyphenylenes  | 530-590 | 510-560 |
| Polyperchlorophenylene | 490 | |
| Polyperfluorophenylenes | 620-720 *) | |
| Polyphenols (from cationic oxid. pol. of phenolic compounds) | 190-440 | |

*) Most of these polymers also had an early and often ill-defined weight loss in the 200-400°C range.

The polyphenylenes under investigation mostly were ill-defined and/or of low molecular weight, with the possible exception of the phenylated polyphenylenes. In most cases, the TGA curves are equally ill-defined, making it difficult to establish onsets of degradation. The Tdec's scatter widely.

From the available data, TGA curves have been "constructed" which represent the optimal weight loss behavior of the four most important polymers of this class (Figure 5). The curves show that in spite of the higher Tdec of polyperfluorophenylene, the non-fluorinated polyphenylenes seem to perform as well as the former below 700°F. For all <u>practical</u>

purposes, one may conclude that optimal polyphenylenes and polyperfluorophenylenes are equal in stability, while phenylated polyphenylenes are about 100°C less stable.

Tdec's (Air) have been established with reasonable degrees of reliability only for the phenylated polyphenylenes. They are about 20 to 30°C below the Tdec's ($N_2$).

References used: 15-17.

Sources of Polymers:

AFML

Case Inst. of Technology

GEC

Hughes

Monsanto

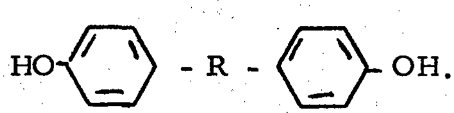
University of Illinois

12. Phenol-Formaldehyde Resins

A wide variety of phenol-formaldehyde resins, cured with various curing agents, has been evaluated. The Tdec's ($N_2$), which often were ill-defined, scattered between 280 and 540°C. Since the exact structure was not known to us in all of the cases, no further conclusions can be drawn from these results. The Tdec's (Air), as far as determined, were practically identical to Tdec ($N_2$).

Linking groups between phenylenes.

Learmonth and Marriott (Ref. 18) studied the thermal degradation (vacuum 0.05 mm, $\Delta T$ = 600°C/hr) of phenolic resins synthesized from




The following order of Tdec's can be derived from their TGA curves:

| R: | Tdec ($N_2$) |
|---|---|
| - $C(CF_3)_2$ - | 390 |
| - $CH_2$ - | 360 |
| - $CH(CH_3)_2$ - | 320 |
| - $C(CF_2Cl)_2$ - | 260 |

Source of Polymers:

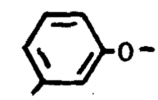
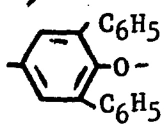
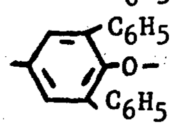
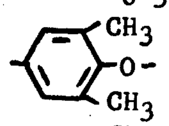
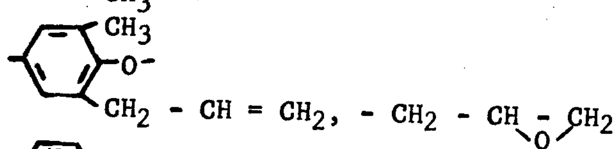
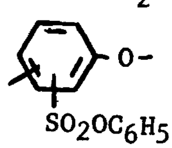
Monsanto

Dow Chemical

Unknown Sources

13. <u>Polyphenylene Oxides</u>

a. Effect of Substituents.

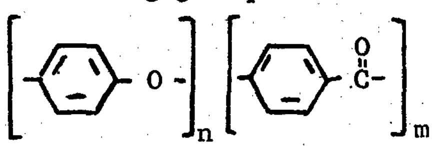
| | Tdec ($N_2$) | Tdec (Air) |
|---|---|---|
|   | 570 | 560 |
|   | 510 | 460 |
|   , chlorinated | 485 | 500 |
|   | 430 | 440 |
|   | 390 | |
|   | 290 | |
| - $OCH_3$ | 240 | |
| - OH | 220 | |
| - $SO_3H$ | 190 | |
| - $SO_2$ | 190 | |

From the above table, the following order of stability of the various substituents can be derived, if one disregards the position in the ring:

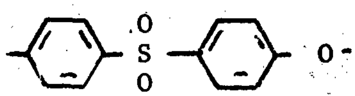
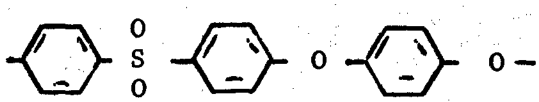
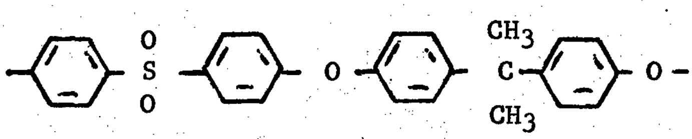
$$-H > -C_6H_5 > -CH_3 > \begin{matrix} -CH_2-CH=CH_2 \\ -CH_2-\underset{\diagdown\,O\,\diagup}{CH-CH_2} \end{matrix} > -SO_2OC_6H_5 > -OCH_3$$

$$> -OH > \begin{matrix} -SO_3H \\ -SO_2Cl \end{matrix} .$$

b. Linking groups between Phenylenes (other than -O-).

 Tdec ($N_2$): 510

In addition to above results determined in our laboratory, Hale and coworkers (Ref. 19) reported TGA data which allow the determination of the following Tdec's ($\Delta T = 600°C/hr$):

| | Tdec(Argon) *) | Tdec(air) *) |
|---|---|---|
|  | 530 | 560 |
|  | 570 | 570 |
|  | 520 | 520 |

Above results suggest the following order of stability:

$$-O- \; > \; -CO-$$

$$-O- \; > \; -SO_2- \; > \; -\overset{CH_3}{\underset{CH_3}{\overset{|}{\underset{|}{C}}}}-$$

*) Comparison of the results of one of Hale's polymers with one of ours (see under XV. Polyphenylene Sulfones) shows Hale's Tdec's to be about 50°C higher than ours, probably as a result of the higher heating rate.

c. Air versus inert atmosphere.

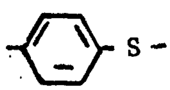
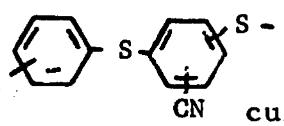
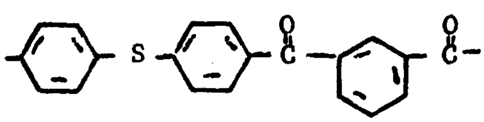
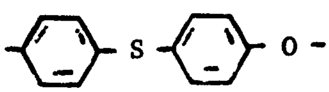
The Tdec (Air) of most of our polymers and those found in the literature, was about the same as Tdec ($N_2$).

Figure 6 shows TGA curves of Poly-2,6-dimethylphenylene oxide.

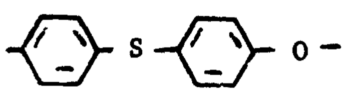
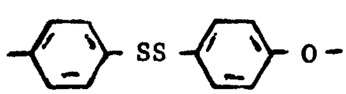
Sources of Polymers:

- AFML
- Borden Chemical
- GEC
- University of Arizona
- Whittaker

14. Polyphenylene Sulfides

| | Tdec ($N_2$) | Tdec (Air) |
|---|---|---|
|  | 430-490 *) | 430-490 *) |
|  | 440-540 *) | |
| " cured through CN group | 445-510 *) | |
|  | 490 | 495 |
|  | 410 | 420 |

Results by Fudisawa and Kakutani (Ref. 20; heating rate not listed) indicate:

| | Tdec ($N_2$) | Tdec (Air) |
|---|---|---|
|  +15%  | 420 | 435 |

While the introduction of a nitrile group into a polyphenylene sulfide does not seem to affect stability, crosslinking through this group, which supposedly introduces s-triazine rings decreases Tdec to some extent in most of the

*) Range found for several polymers of the same structure.

individual cases.

Above listings suggest the following order of <u>stability of linkages between phenylenes</u>:

$$\underline{-S- = -\overset{O}{\overset{\|}{C}}- > -O-}$$

<u>Tdec (Air)</u> is about the <u>same as Tdec ($N_2$)</u>.

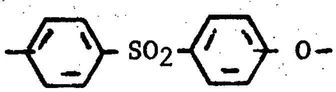
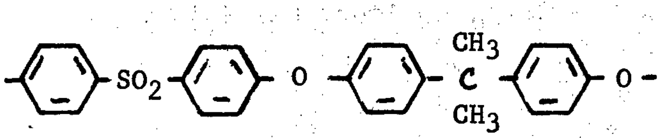
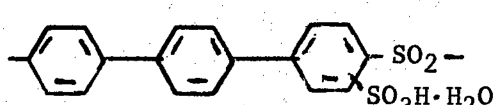
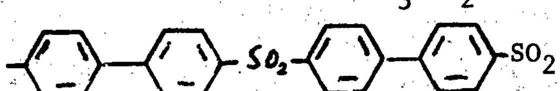
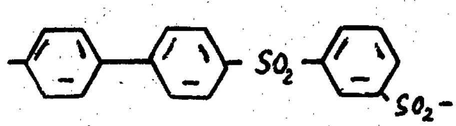
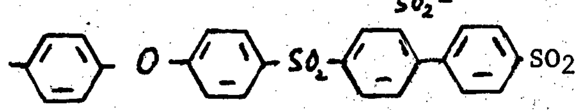
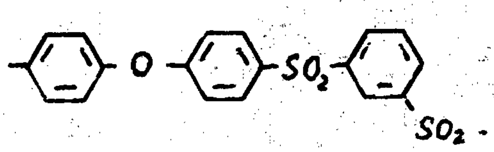
A TGA curve of poly-p-phenylene sulfide is shown in Figure 7.

Sources of Polymers:

Dow Chemical

University of Arizona

15. <u>Polyphenylene Sulfones</u>

| | | Tdec ($N_2$) | Tdec (Air) |
|---|---|---|---|
| |   | 505 | 490 |
| |   | 465 | 460 |
| essentially |   | 460 | |
| essentially |   | 470 | |
| essentially |   | 440 | |
| essentially |   | 440 | |
| essentially |   | 410 | |

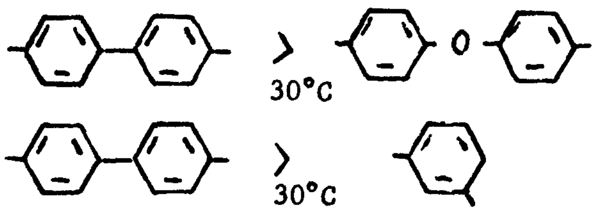
A major part of results on polysulfones available to us has not been used since the polymers were either of low molecular weight, of ill-defined structure or had a variety of linkages. A few polymers with sulfone linkages have been discussed already under 13. Polyphenylene Oxides.

Above results, and comparison with data listed earlier, lead to the following conclusions:

- $SO_2$ - $\geqq$ 460

- $SO_2$ - = - O - > $-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-$

- $SO_2$ - > - S -



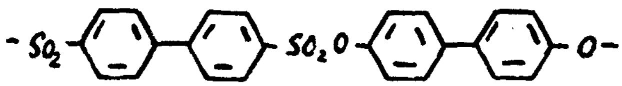
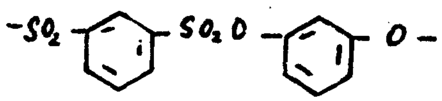
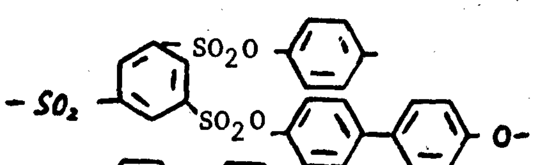
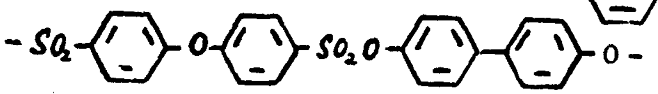
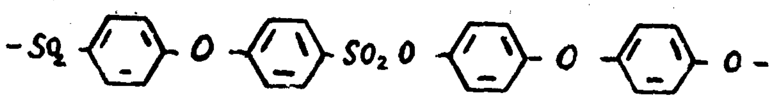
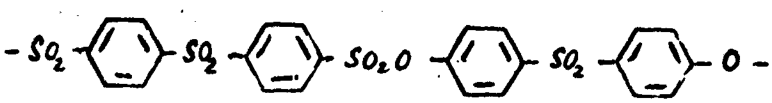
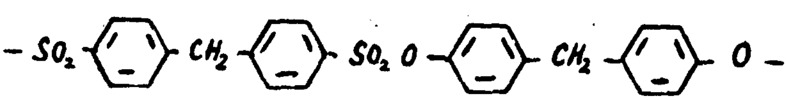
Tdec (Air) has been determined in only two cases and was slightly lower than Tdec ($N_2$).

Figure 8 shows TGA curves of a polyphenyleneether sulfone.

Sources of Polymers:

AFML
Union Carbide
University of Arizona

16. Polysulfonates

| | Tdec ($N_2$) |
|---|---|
|  | 310 |
|  | 325 |
|  | 350 |
|  | 315 |
|  | 300 |
|  | 300 |
|  | 280 |

It has been shown previously (Ref. 21) that the low Tdec of 300 to 325°C can be attributed to the $-SO_2-O-$ linkage. Within this temperature range a very sharp and sudden weight loss occurs as the result of formation of $SO_2$. Presence of -O- or $-SO_2-$ linkages is of no effect, but the methylene moiety seems to reduce the stability, and crosslinking increases it by 25 to 40°C.

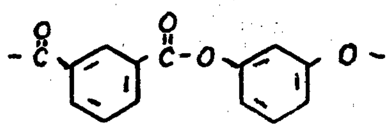
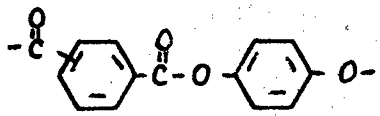
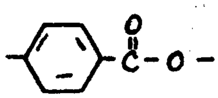
Tdec (Air), determined in only one case, was slightly lower than Tdec ($N_2$).

TGA curves of a polysulfonate are given in Figure 9.

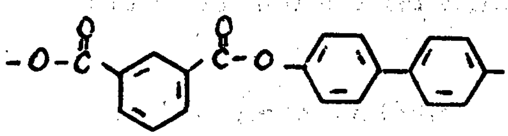
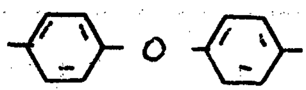
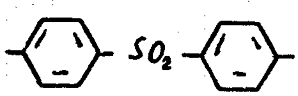
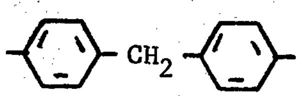
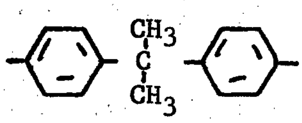
Source of Polymers:

AFML

17. Aromatic Polyesters

| | Tdec ($N_2$) |
|---|---|
|  | 430 |
|  | 460 |
|  | 480 |

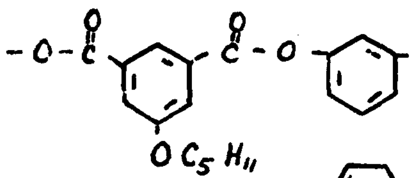
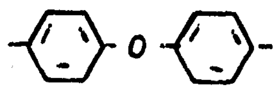
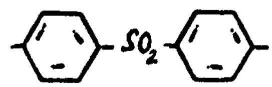
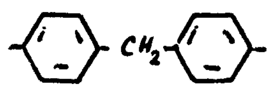
Increased stability with increasing para-orientation can be concluded from these data.

| | | Tdec ($N_2$) |
|---|---|---|
|  | | 430 |
| " |  | 470 |
| " |  | 410 |
| " |  | ~450 |
| " |  | 430 |
| " | $-(CH_2)_2-$ | 370 |

The Order of Stability of linkages between phenylene groups is:

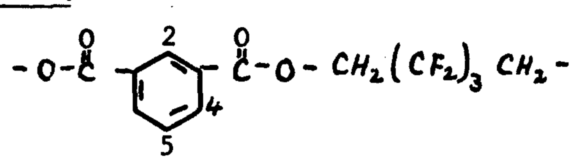
$$-O- > -CH_2- > - > -\overset{CH_3}{\underset{CH_3}{\overset{|}{\underset{|}{C}}}}- > -SO_2- > \text{alkylene chains}$$

without phenylenes.

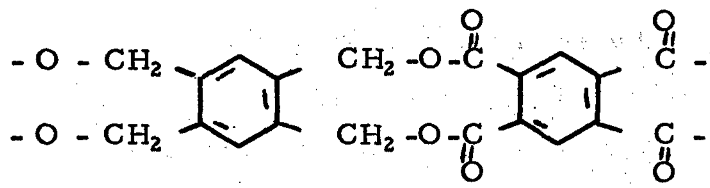
| | | Tdec ($N_2$) |
|---|---|---|
|  | | 400 |
| " |  | 430 |
| " |  | 410 |
| " |  | 380 |
| " |  | 390 |
| " | $-(CH_2)_5-$ | 350 |

From this series, the following order of stability for the linkages can be derived:

$- > -O- > -CH_2- > -SO_2- >$ alkylene chain without phenylenes.

| | | Tdec ($N_2$) |
|---|---|---|
|  | | 450 |
| 5 subst. $-OC_5-H_{11}$ | " | 435 |
| 4 subst. $-OC_5-H_{11}$ | " | 390 |
| 2 subst. $-OC_5-H_{11}$ | " | 390 |

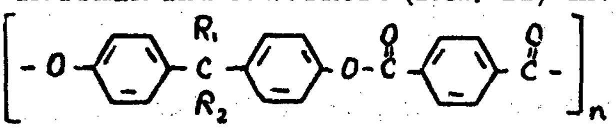
The data above suggest: un subst. > 5-subst. > 4-subst. = 2-subst.



Tdec ($N_2$)

260

The stability of this aliphatic-aromatic polyester is lower than that of purely aliphatic polyesters. However, gradual loss beginning at 80°C suggests incomplete double strand structure and pendant, functional groups. Korshak and coworkers (Ref. 22) investigated polyarylates of the type



and found the following stabilities for $-\overset{R_1}{\underset{R_2}{C}}-$ :

| | Tdec ($N_2$) |
|---|---|
| $-CH_2-$ | 375 |
| $-C(CH_3)_2-$ | 397 |
| $-C(CF_3)_2-$ | 438 |
| $-CH(C_6H_5)-$ | 419 |
| $-C(CH_3)(C_6H_5)-$ | 434 |
| $-C(CF_3)(C_6H_5)-$ | 446 |
| $-C(C_6H_5)_2-$ | 442 |

The order of stability:

$$-\overset{CF_3}{\underset{C_6H_5}{C}}- > -\overset{C_6H_5}{\underset{C_6H_5}{C}}- > -\overset{CF_3}{\underset{CF_3}{C}}- > -\overset{CH_3}{\underset{C_6H_5}{C}}- > -\overset{H}{\underset{C_6H_5}{C}}- >$$

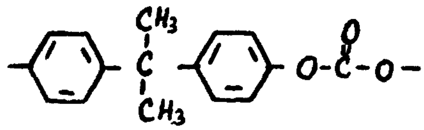
$$-\overset{CH_3}{\underset{CH_3}{C}}- > -CH_2-$$ suggests that increasing polarity and bulkiness of $R_1$ and $R_2$ increases chain rigidity and stability.

TGA curves of an aromatic polyester are shown in Figure 10.

Sources of Polymers:

- AFML
- Carborundum
- Dupont
- GEC
- Koppers

18. Polycarbonates



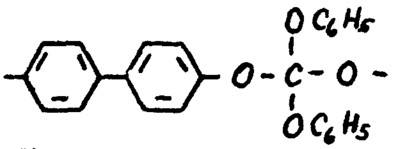
Tdec ($N_2$)

430

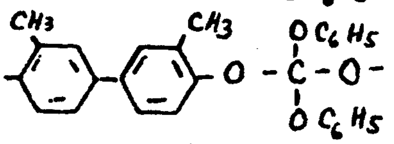
Decomposition studies (Ref. 23) show that the - $O-\overset{O}{\overset{\|}{C}}-O$ - linkage breaks before the $-\underset{CH_3}{\overset{CH_3}{C}}-$ linkage does, so that the Tdec of 430°C can be attributed to the carbonate moiety.

Studies by Takekoshi (Ref. 24) suggest the following order of stability for another carbonate system:

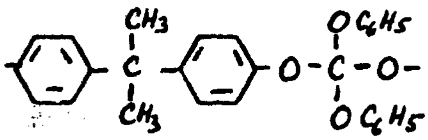
Tdec ($N_2$)



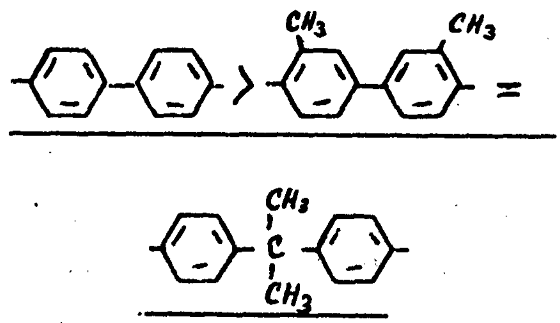
380



360

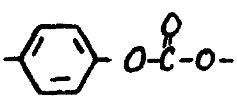


360

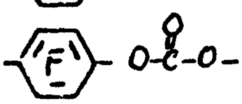


Lynch and coworkers (Ref. 25) determined the stability of polycarbonates in air at 60°C/hr:

Tdec (Air)



420

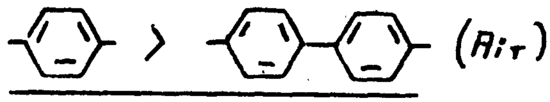


310

Perfluorinated polycarbonates are less stable than the corresponding aromatic polycarbonates in air. Also:

360

240



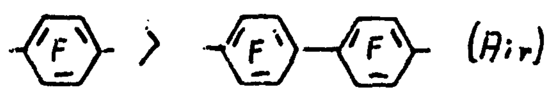
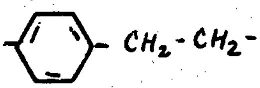
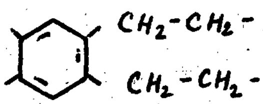
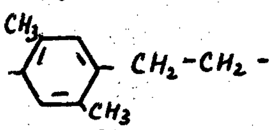
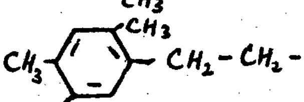
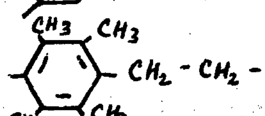
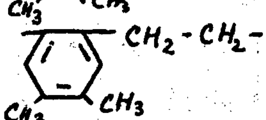
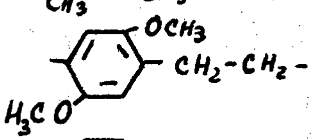
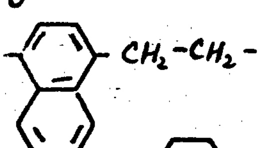
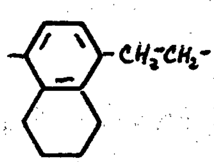
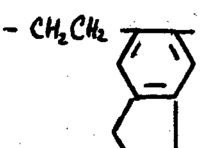



Figure 11 shows a TGA curve of Poly [2,2-propane-bis (4 phenyl carbonate)] .

Source of Polymers:

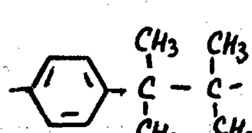
GEC

19. Polyxylylenes

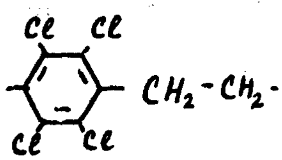
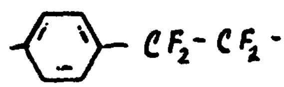
| | Tdec ($N_2$) |
|---|---|
|  | 430 |
|  | 380 |
|  | 400 |
|  | 440 |
|  | 440 |
|  | 390 |
|  | 370 |
|  | 390 |
|  | 390 |
|  | 390 |

The dominant decomposition reaction of the polyxylylenes is the formation of chain fragments (Ref. 26), and comparison of the results suggests that the <u>breakdown of the $-CH_2-CH_2-$ linkage occurs in the range of 380 to 440°C</u>. The scattering of data probably is not the result of true differences in stability. There seems to be no significant difference between O-, m- and p- substitution, single or double strand (although the latter retain more residue at 900°C), unsubstituted, methyl- or methoxy substituted rings and the replacement of phenylene by naphthalene or indene.

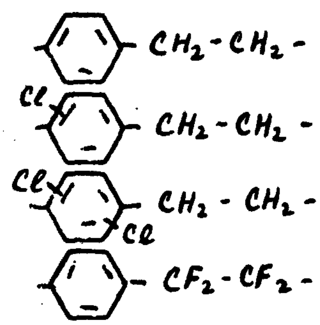
While methyl in the aromatic ring is without influence on the stability, the <u>stability is decreased considerably when methyl is introduced into the $-CH_2-CH_2-$ linkage:</u>

| | Tdec ($N_2$) |
|---|---|
|  | 250 |

On the other hand, <u>aromatic chlorines and aliphatic fluorines increase the stability</u>:

| | Tdec ($N_2$) |
|---|---|
|  | 500 |
|  | 535 |

This has been essentially confirmed by Joesten (Ref. 27):



| Tdec ($N_2$) | Tdec (Air) |
|---|---|
| 470 | 280 |
| 500 | 280 |
| 470 | 320 |
| 540 | 520 |

While the Tdec's for the chlorine containing polymer are the same or only slightly higher than the chlorine-free polyxylylenes, a distinct increase of Tdec ($N_2$) and Tdec (Air) occurs with the introduction of aliphatic fluorine. These findings are remarkable in the light of the decreased stability of poly $\alpha\beta\beta$-trifluorostyrene in comparison to polystyrene:

| | Tdec ($N_2$) | Tdec (Air) |
|---|---|---|
| $- CF - CF_2 -$  | 315 | 330 |

TGA curves of the fluorinated polyxylylene are shown in Figure 12.

Sources of Polymers:

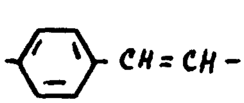
AFML

Union Carbide

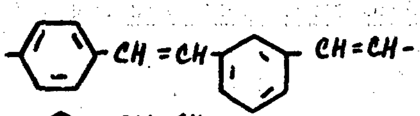
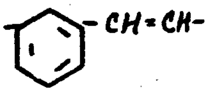
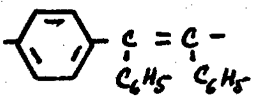
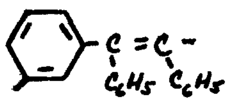
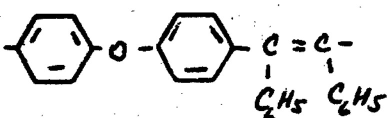
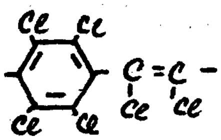
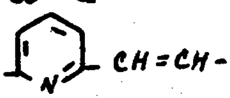
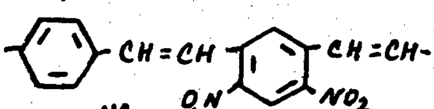
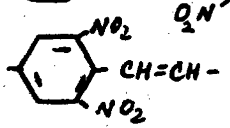
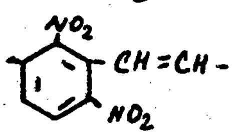
U. S. Industrial Chemicals

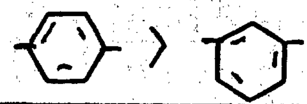
U. S. Rubber

20. <u>Polyxylylidenes</u>

| | Tdec ($N_2$) |
|---|---|
|  | 500 |

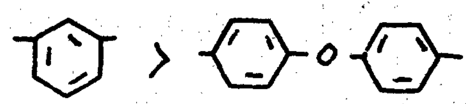
From the results, it can be concluded:

| | Tdec ($N_2$) |
|---|---|
|  | 310 |
|  | 270 |
|  | 500-535 |
|  | 470 |
|  | 450 |
|  | 570 |
|  | 210 |
|  | 260 |
|  | 160 |
|  | 180 |



although it is difficult to explain the magnitude of difference between the first three results. Also:

$$-\underset{C_6H_5}{\overset{|}{C}} = \underset{C_6H_5}{\overset{|}{C}} - \;\geqq\; -CH=CH-$$

and: 

Complete chlorination increases Tdec considerably, although the polymer loses weight already above 100°C, and the residual weight at 900°C is low. Pyridine in the chain, and nitro groups, decrease Tdec substantially.

A TGA curve of a polyxylylidene is shown in Figure 12.

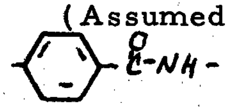
Sources of Polymers:

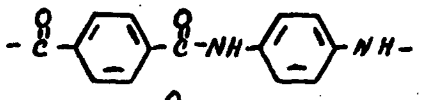
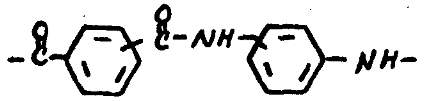
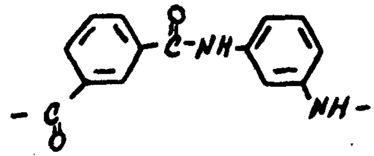
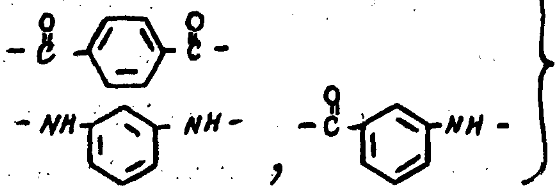
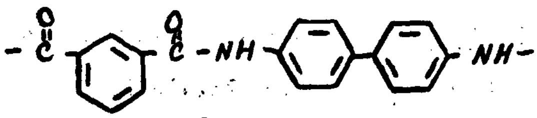
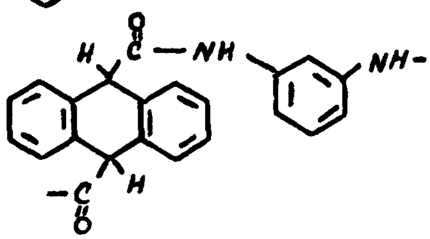
AFML

U. S. Industrial Chemicals

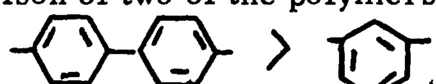
U. S. Rubber

## 21. Aromatic Polyamides

| (Assumed Structures) | Tdec ($N_2$) | Tdec (Air) |
|---|---|---|
|  | 510 | 510 |
| " | 600 | 530 |
| " | 570 | 525 |

| (Assumed Structures) | Tdec ($N_2$) | Tdec (Air) |
|---|---|---|
|  | 470 | 490 |
|  | 565 | 520 |
|  | 410 | |
| 〃 | 390 | 475 |
| polymer containing:  | 380 | 430 |
|  | 500 | 490 |
|  | 340 | |

Most of the polymers shown here were in the form of fibers or films. Uncertainty about the exact structure, posttreatment, sizing and additives may account for a scattering of the results, as is demonstrated by the wide range of Tdec's for the first structure. Nevertheless, there seems to be a trend toward lower stability in nitrogen and in air for less rod-like and less regular structures. Comparison of two of the polymers also suggests

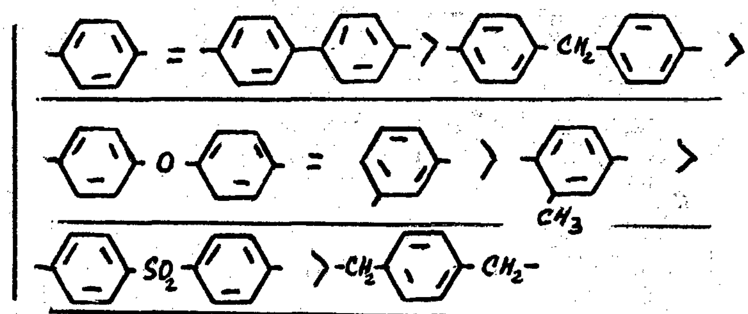


No particular pattern for Tdec (Air) in comparison to Tdec ($N_2$) can be recognized.

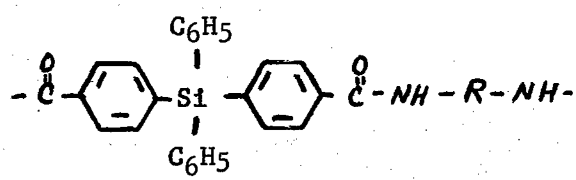
Of the large amount of literature data on polyamides, only those have been used which allow ready comparison of structures. Heating rates often are not given, or different from ours, therefore absolute values will not be presented here, but only orders of stability.

(reference 28)

Order of stability of R:



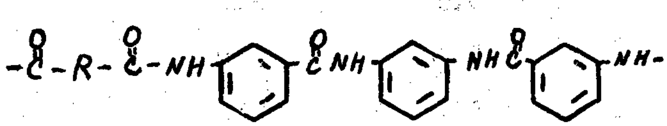
Tdec (diff), the difference between the highest and lowest Tdec, is ~65°C.



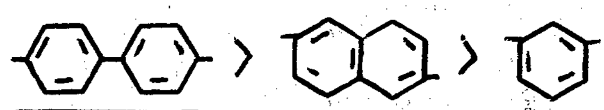
(reference 29)

Order of stability of R:

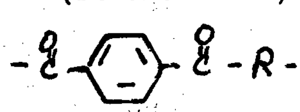
Tdec (diff) = 25°C



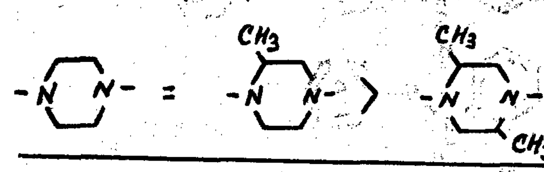
(reference 30)



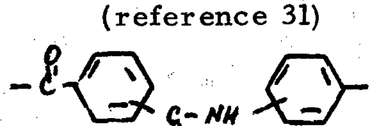
Tdec (diff) = ~70°C



(reference 31)



Tdec (diff) = ~55°C



(reference 32)

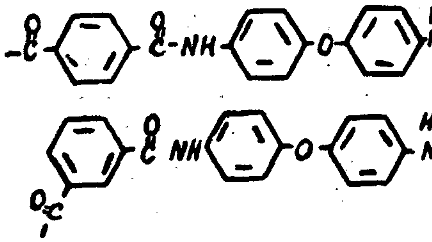
General trend:

-p- > -m- > -o-

Tdec (diff) = 200°C

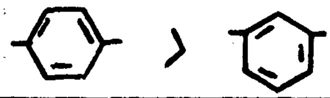
This trend (-p- > -m- > -o-) has been confirmed by results obtained by Dine-Hart and coworkers (reference 33).

The following information about comparative stabilities in <u>air</u> has been found ($\Delta T = 180°C/hr$, Ref. 34):



| | Tdec (air) |
|---|---|
| (first structure) | 350 |
| (second structure) | 320 |

Therefore:



(air)

TGA curves of a polyamide are shown in Figure 13.

Sources of Polymers:

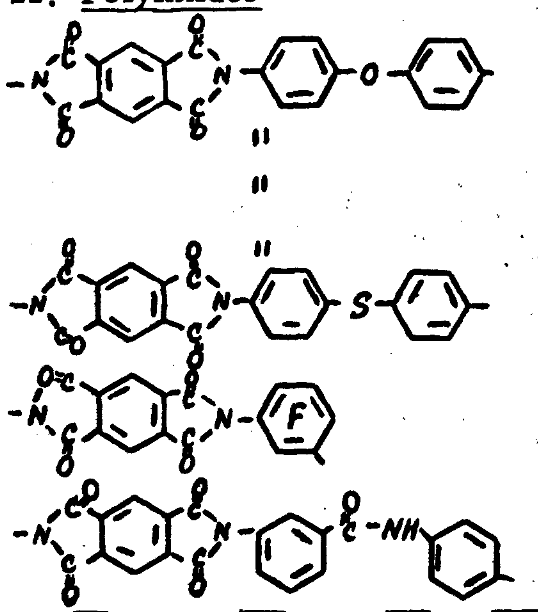
AFML

Chemstrand

Dupont

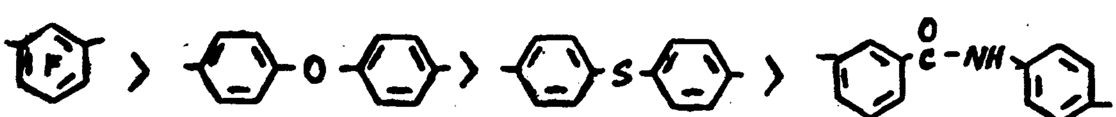
University of Arizona

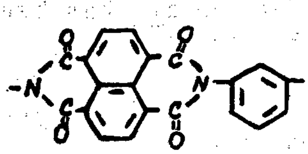
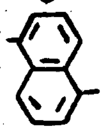
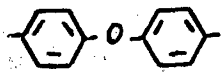
22. <u>Polyimides</u>



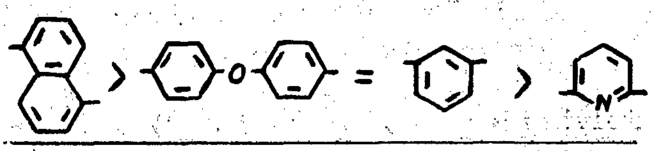
| Tdec ($N_2$) | Tdec (air) |
|---|---|
| 510 | 5[illegible]0 |
| 555 | 530 |
| 570 | 550 |
| 535 | 490 |
| 520 | 520 |
| 590 | 580 |
| 460 | 460 |

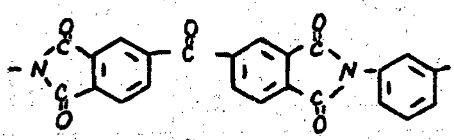
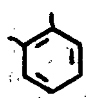
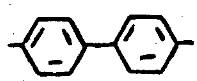
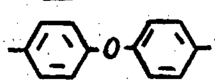
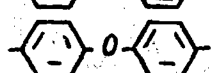
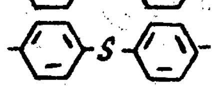
The results suggest the following order of stability for nitrogen and air:



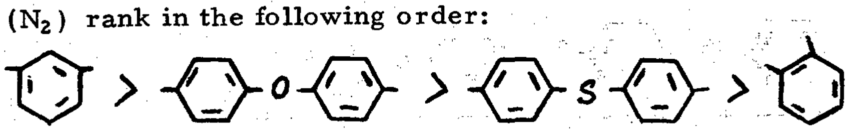
| | Tdec ($N_2$) | Tdec (air) |
|---|---|---|
|  | | 540 |
| "   " | 555 | 520 |
| "  | | 460 |
| "  | 600 | 480 |
| "  | 560 | 520 |
| "  | 470, 550 | 420, 560 |

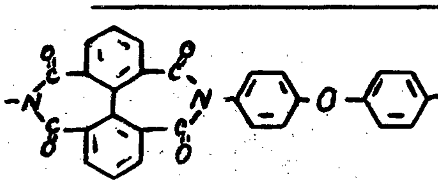
The order for Tdec ($N_2$) is:



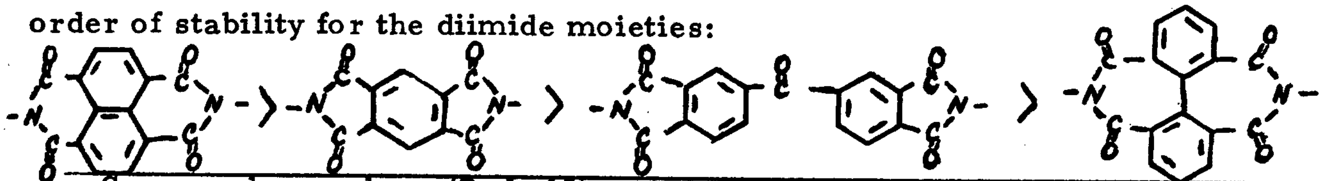
| | Tdec ($N_2$) | Tdec (air) |
|---|---|---|
|  | 540 | 570 |
| "   " | 475 | 475 |
| "  | ~470 | ~425 |
| "  | | ~500 |
| "  | 500 | 510 |
| "  | 510 | |
| "  | 475 | 525 |
| "  | | 460 |

Tdec's ($N_2$) rank in the following order:

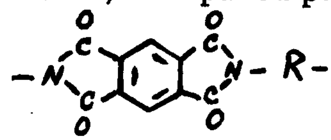


| | Tdec ($N_2$) | Tdec (air) |
|---|---|---|
|  | 410 | 420, 490 |

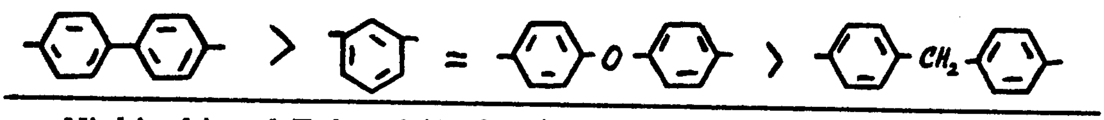
Comparing the polymers with the diphenylether moiety results in the following order of stability for the diimide moieties:



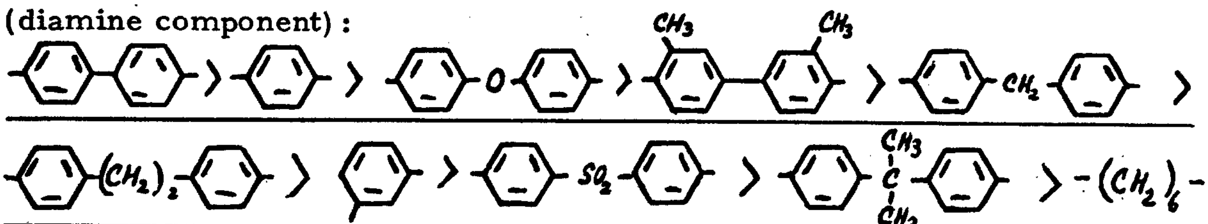
Sroog and coworkers (Ref. 35) compared polyimides of this type



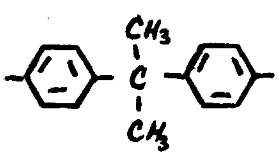
in helium. Tdec's derived from their data show for R:



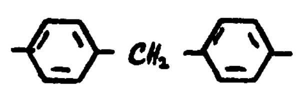
Nishizaki and Fukami (Ref. 36) determined the thermal stability of polypyromellitimides in helium and air with the following results for Tdec ($H_2$) (diamine component):



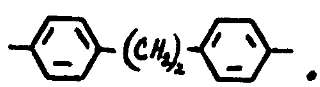
The order of stability in air is similar except for a higher ranking of



and a lower of

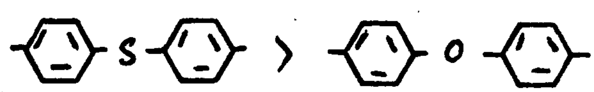


and



From a study by Tokarev and coworkers (Ref. 37), it can be concluded:

Tdec (air) :



TGA curves of a polyimide are shown in Figure 14.

Sources of Polymers:

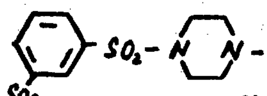
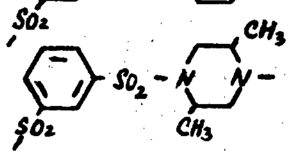
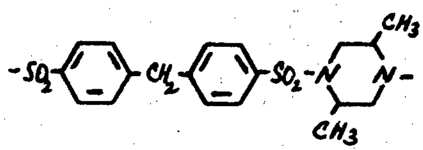
AFML

Dupont

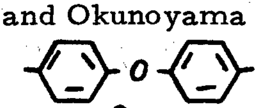
Monsanto

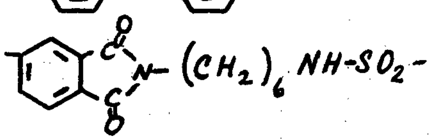
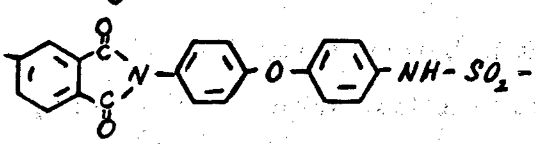
Westinghouse

23. Polysulfamides

| | Tdec ($N_2$) |
|---|---|
|  | 350 |
|  | 315 |
|  | 360 |
|  | 310 |

The major breakdown is sharp and rapid (see Figure 15), the formation of $SO_2$ probably being the major contribution. Tdec ($N_2$) and Tdec (air) of the basic sulfamide-pyrimidine system is in the order of 350 to 360°C, for the methyl- substituted pyrimidine systems 35 to 50°C lower.

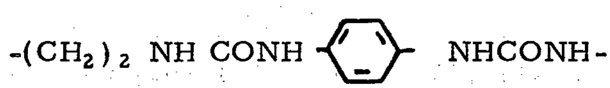
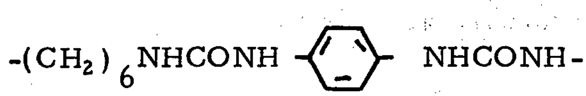
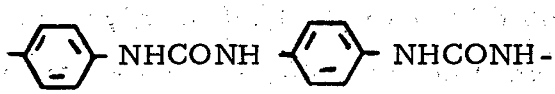
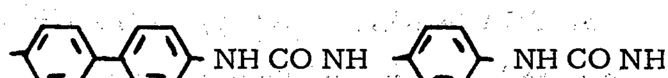
Imai and Okunoyama (Ref. 38) found 35 to 55°C lower stabilities replacing  by - $(CH_2)_6$ - ($\Delta T$ = 300°C/hr):

| | Tdec ($N_2$) | Tdec (air) |
|---|---|---|
|  | 330 | 310 |
|  | 365 | 365 |

Source of Polymers:

AFML

24. Polyureas

| | Tdec ($N_2$) | Tdec (air) |
|---|---|---|
|  | 250 | |
|  | 270 | |
|  | 330 | |
|  | 330 | 340 |
|  | 370 | |

It is believed that the primary breakdown occurs at the urea linkage. However, its Tdec varies widely depending upon the linking moiety. The following order of stability for these moieties can be derived from the above:

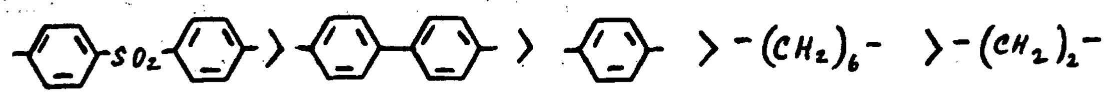


Figure 16 shows the TGA curve of a polyurea.

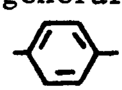
Source of Polymers:

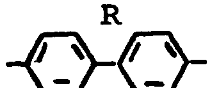
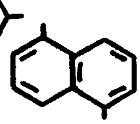
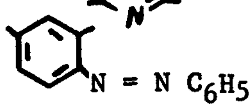
AFML

25. Polymeric Schiff Bases

The information about this class of polymers has been derived exclusively from literature TGA data and curves.

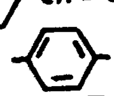
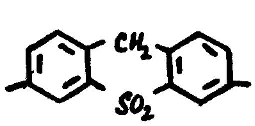
Data by Delman and coworkers (Ref 39) ($\Delta T$ = 180°C/hr) yield the following Tdec's for a general structure

 CH = N - R - N = CH - :

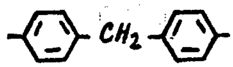
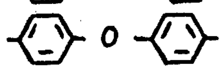
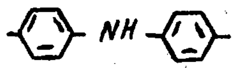
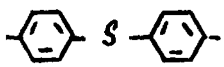
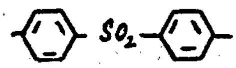
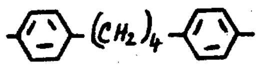
| R | Tdec ($N_2$) |
|---|---|
|  | 480 |
|  | 440 |
|  | 380 |
| — | 370 |
|  | 360 |
|  | 240 |

It is believed that the low Tdec of 240°C for the last moiety in the listing has to be attributed to the -N = N- group.

Results by D'Alelio and coworkers (Ref. 40) ($\Delta T$ = 900°C/hr) suggest the following Tdec's for the same polymer structure as above:

| R | Tdec ($N_2$) |
|---|---|
|  | 570 |
|  | 520 |
|  | 520 |
|  | 510 |

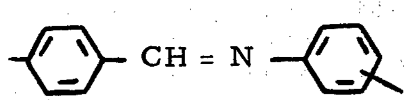
It should be noted that these polymers have been cured to 400°C. This and the high TGA heating rate may be the reason for the high level of Tdec's, and the small difference between the Tdec's of the various aromatic moieties. The high

| R | Tdec ($N_2$) |
|---|---|
|  | 500 |
|  | 500 |
|  | 500 |
|  | 500 |
|  | 490 |
|  | 490 |
| $-(CH_2)_4-$ | 375 |
| $-CH_2)_6-$ | 360 |

curing temperature very likely introduced structural changes, for example <u>extensive crosslinking</u>, into the polymers, which contribute more to the stability than individual moieties.

The following data have been found about the effect of o- versus m- versus p- substitution:

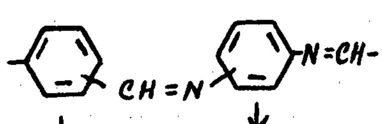
Delman and coworkers (Ref. 39), $\Delta T = 180°C/hr$:



| N = CH- | Tdec ($N_2$) |
|---|---|
| - p - | 440 |
| - m - | 450 |
| - o - | 460 |

These data would suggest: <u>o > m > p</u>.

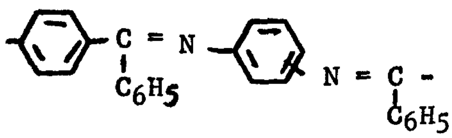
D'Alelio and coworkers (Ref. 41), $\Delta T = 900°C/hr$:



| | | Tdec ($N_2$) |
|---|---|---|
| - p - | - p - | 500 |
| - p - | - m - | 570 |
| - m - | - p - | 500 |
| - m - | - m - | 550 |

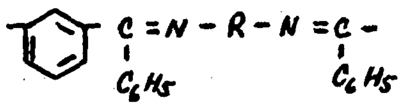
By comparing suitable pairs of polymers, there is a slight trend towards <u>m > p.</u>

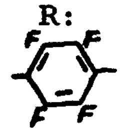
Kaufman and coworkers (Ref. 42), $\Delta T = 360°C/hr$:



| | | $T_{dec}(N_2)$ | $T_{dec}$ (air) |
|---|---|---|---|
| -p- | -p- | 500 | 500 |
| -p- | -m- | 490 | 500 |
| -p- | -0- | 450 | 490 |
| -m- | -p- | 470 | 500 |
| -m- | -m- | 480 | 470 |
| -m- | -0- | 450 | 400 |

In nitrogen and in air, the general trend is p > m > 0.

Finally, data by Volpe and coworkers (Ref. 43), $\Delta T$ = 360°C/hr, give the following Tdec's: 

| R: | $T_{dec}$ ($N_2$) | $T_{dec}$ (air) |
|---|---|---|
|  | 450 | 440 |
|  | 420 | 400 |

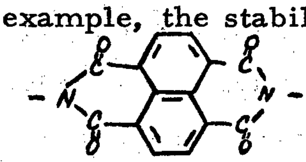
Thus, for perfluorophenylene: -p - > -m -.

## SECTION II: CONCLUSIONS

In this section an attempt has been made to reduce the amount of information given in the Discussion to the essential facts and to consolidate, simplify and average the often contradictory results.

In Table I, the maximum stabilities obtained for various polymers and moieties have been listed, based on our own data only. For the purpose of clarity and significance, some of the results have been slightly adjusted to eliminate obviously unrealistic differences between data, and only structures of some significance are shown in this table. The Tdec figures in this table should represent, or come close to, the stability of a system in question under optimum conditions, such as high molecular weight, freedom from impurities and weak links. While the ranking shows the prominent position of perfluorinated aromatics and aliphatics, it should be pointed out that we have not yet seen a polyperfluorophenylene which has not, in addition to a major breakdown at 720°C, also a substantial weight loss at lower temperatures.

To arrive at the data presented in Tables II and III, the order of stability of linking groups and of aromatic units has been compared, whenever possible, in series of polymers; for example, the stability of polyimides with the



moiety and different aromatic linking units has been compared. A list of these stability rankings from a variety of polymer systems has been compiled and the results from over 30 comparative rankings (which showed vast discrepancies) have been averaged. This could be done only in a rather crude fashion since each set of data contained different sets of moieties.

In addition to the information in Tables I to III, the following conclusions can be drawn:

Stability in Air. While it is known that oxidative attack on polymer molecules may occur well below Tdec, as indicated by oxygen uptake and slight weight gain, the Tdec's (Air) of most of the polymers under investigation were in the same order of magnitude as the Tdec's (inert).

That means that the onset of the major cleavage reactions was essentially thermal and at that point not affected by the presence of oxygen. This is demonstrated in Table IV, which contains the average relationship of Tdec (air) versus Tdec (inert) *) for those classes of polymers for which TGA (air) data were available. As can be seen, all of the Tdec (air) /Tdec (inert) values are between 0.93 and 1.02 except for the polyxylylenes, with a Tdec (air)/Tdec($N_2$) value of 0.61. In individual cases, the stability in air of polyxylylenes was found to be up to 200°C lower than in nitrogen. It seems that the $-CH_2-CH_2-$ linkage is especially vulnerable to oxygen attack.

Length of the alkylene chain. In aliphatic-aromatic polyureas, in which the urea linkage -NH CO NH- determined the low level of stability, an increase in length of the alkylene chain seemed to enhance the stability slightly, while in more stable polymers, such as the polyimides, increased chain length resulted in reduced stability.

Tacticity. No marked difference seemed to exist between the Tdec's of cis and of trans isomers in natural rubber and guttapercha. For polypropylene oxide, however, the cis isomer was found to be more (30°C) stable than the trans isomer.

Double Bonds. In vinyl polymers, the presence of a double bond in the chain (polybutadiene vs. polyethylene, polyphenylacetylene vs. polystyrene) seems to decrease the stability. In phenylene-R-polymers (polyxylylidenes vs. polyxylylenes) the opposite effect was observed.

Packing. The positive effect of close packing of the polymer chains on the stability is well known. It is evident if one compares polyethylene and polyvinylcarbazol (interlocking) with other vinyl polymers. On the other hand, disruption of symmetry in a copolymer caused a considerable drop in stability. In the aromatic polyamide series, more rodlike and regular structures showed increased stability. In a series of aromatic polyesters, replacement of hydrogen in a $-CH_2-$ moiety with more and more polar and

---

*) Refers to runs in nitrogen, helium and vacuum.

bulky substituents ($-CH_3$, $-CF_3$, $-C_6H_5$) caused stiffening of the chain and increased stability by as much as 70°C.

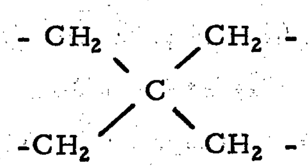
Ortho-meta-para substitution. With a very few exceptions (and these involved structures which were not well defined) it was found:

$$p > m > 0,$$

as was to be expected (see "Packing"). In general, the difference in stability between p- and m- (o-) was 30-50°C, but in isolated cases above 200°C.

Crosslinking. In general, crosslinking increases the stability distinctly. Going from polysytrene to polytrivinylbenzene increases the stability by 55°C. A 45°C increase in stability was found when comparing polytetrafluoroethylene with the ladder structure polyperfluorobutadiene. A stability increase between 25 and 40°C was observed between a linear (1, 4 substituted) and a tridimensional (1, 3, 5-substituted) polyarylsulfonate.

Sidegroups and Branching. In vinyl polymers, the presence of side groups generally reduces stability. Quaternary carbon atoms in the molecule reduce the stability more than tertiary carbon atoms. Pendant methyl groups (polyethylene and polypropylene vs. polymethylene) may decrease the stability by 15-35°C, while branching in a spiro polymer



causes a reduction of 45-85°C. Methyl substitution in the piperazine ring system yields 35-40°C lower stability. Bulky and polar side groups may not be detrimental to stability if they improve (or do not hinder) packing and interlocking, such as the carbazol side group in polyvinyl carbazol, or as sidegroups on the $-CH_2-CH_2-$ and $-CH=CH-$ linkages of polyxylylenes and -xylylidenes. Little effect on the stability was observed if the sidegroup decomposes without affecting the main chain, such as $-CONH_2$ (which forms $-CN$ and $H_2O$) or $-OC_2H_5$ (which forms $-OH$ and $C_2H_4$). Disadvantageous are, for example, $-OH$ and $-Cl$, which abstract hydrogen from the main chain to form $H_2O$ and HCl.

Sidegroups in aromatic rings may increase the stability, as observed for chlorine-substituted polyxylylenes. On the basis of the data we have, only a very general listing can be given on how the sidegroups on aromatic rings affect stability:

Improved to slightly reduced stability: -F, -Cl, $-C_6H_5$, $-CH_3$, -CN, possibly $-NH_2$

Distinctly reduced stability: -OH, $-OCH_3$, -COOR, $-SO_3R$

Very high loss of stability: $-NO_2$ (oxidizes polymer)

Halogen Content. The effect of halogen content has already been discussed under "Sidegroups and Branching". See also Table II. While the level of stability of fluorinated vinyl polymers is much higher than that of chlorinated vinyl polymers, both decrease in stability with the availability and proximity of hydrogen in the polymers, the chlorinated polymers more so than the fluorinated ones. However, other factors are also involved. A considerable difference in stability exists between poly -$\alpha,\beta,\beta$-trifluorostyrene, which seems to unzip and which is of low stability, and poly $\alpha,\alpha,\alpha',\alpha'$- tetrafluoro-p-xylylene, which is very stable and forms polymer fragments on decomposition.

As far as ring chlorination and fluorination is concerned, the effect depends very much upon the polymer system. Perchlorination seems to increase the stability of polyxylylenes and -xylylidenes, and decrease that of polyphenylenes, while chlorination of a polyphenylene oxide resulted in lower stability in nitrogen and higher stability in air. Perfluorination increased the stability of polyphenylenes and decreased the stability of polycarbonates.

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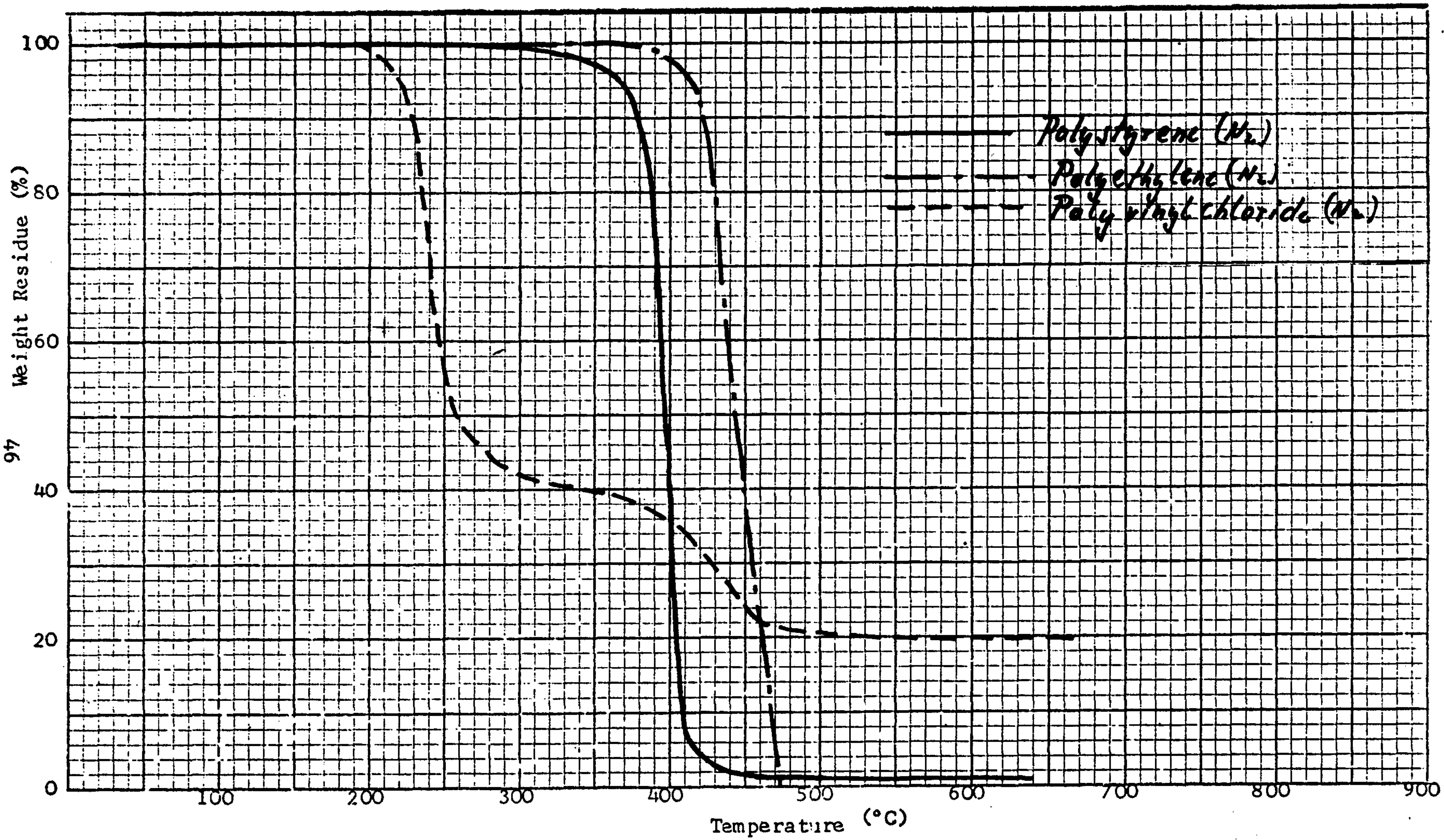



Fig. 1: TGA curves of representative Vinyl Polymers.

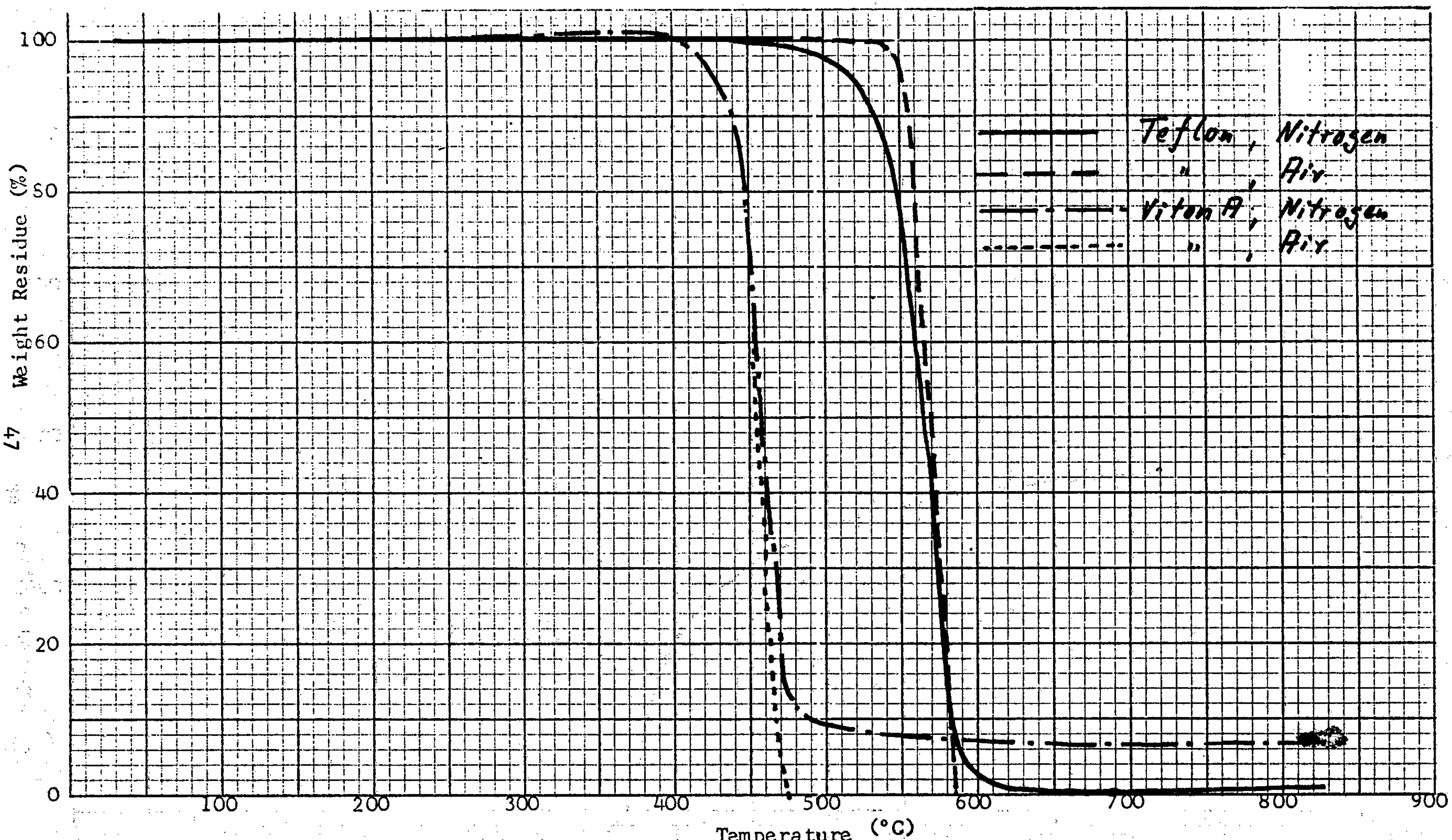



Fig. 2: TGA curves of Teflon and Viton A.

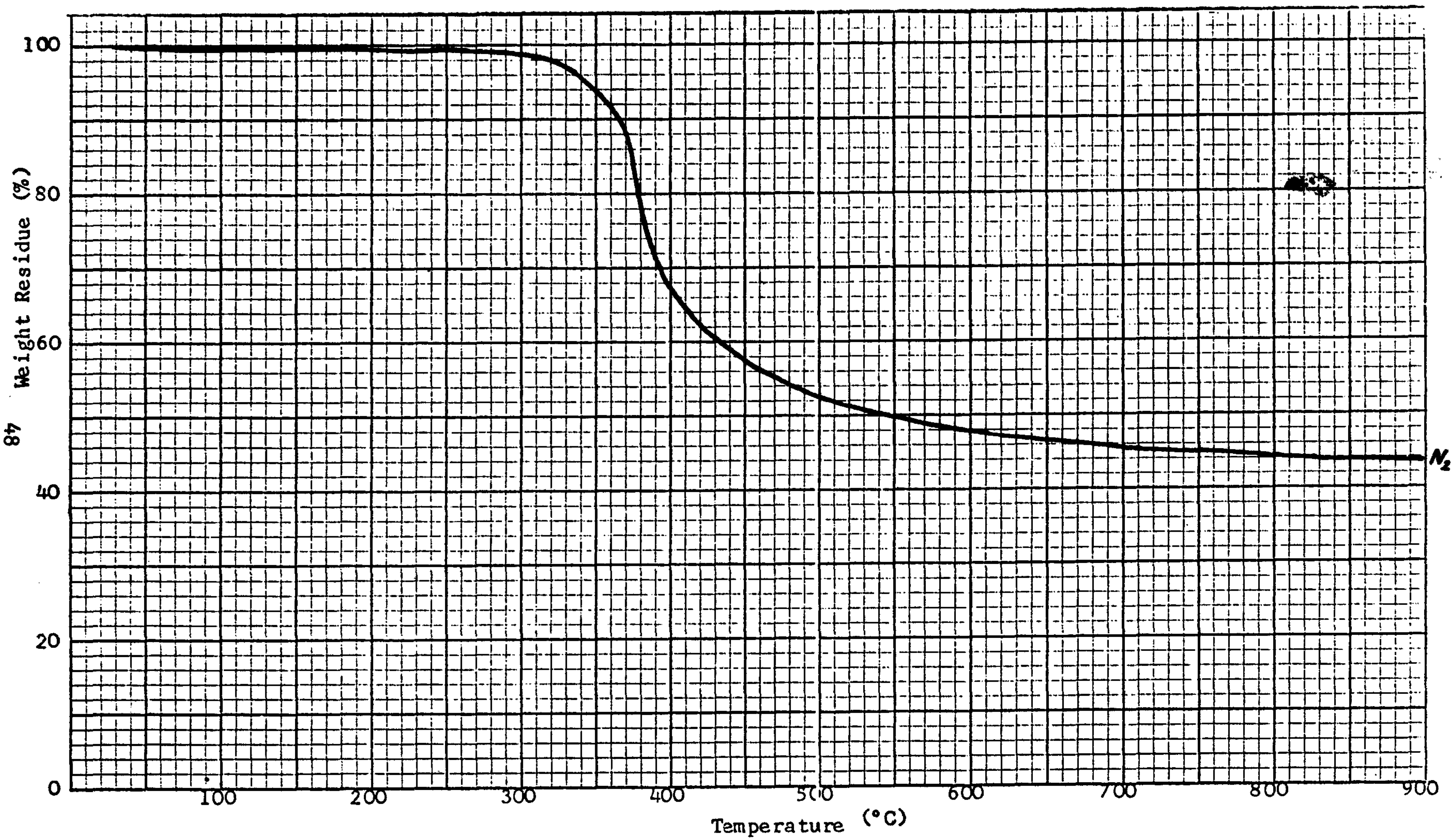



Fig. 3: TGA curve (nitrogen) of Epon 1031.

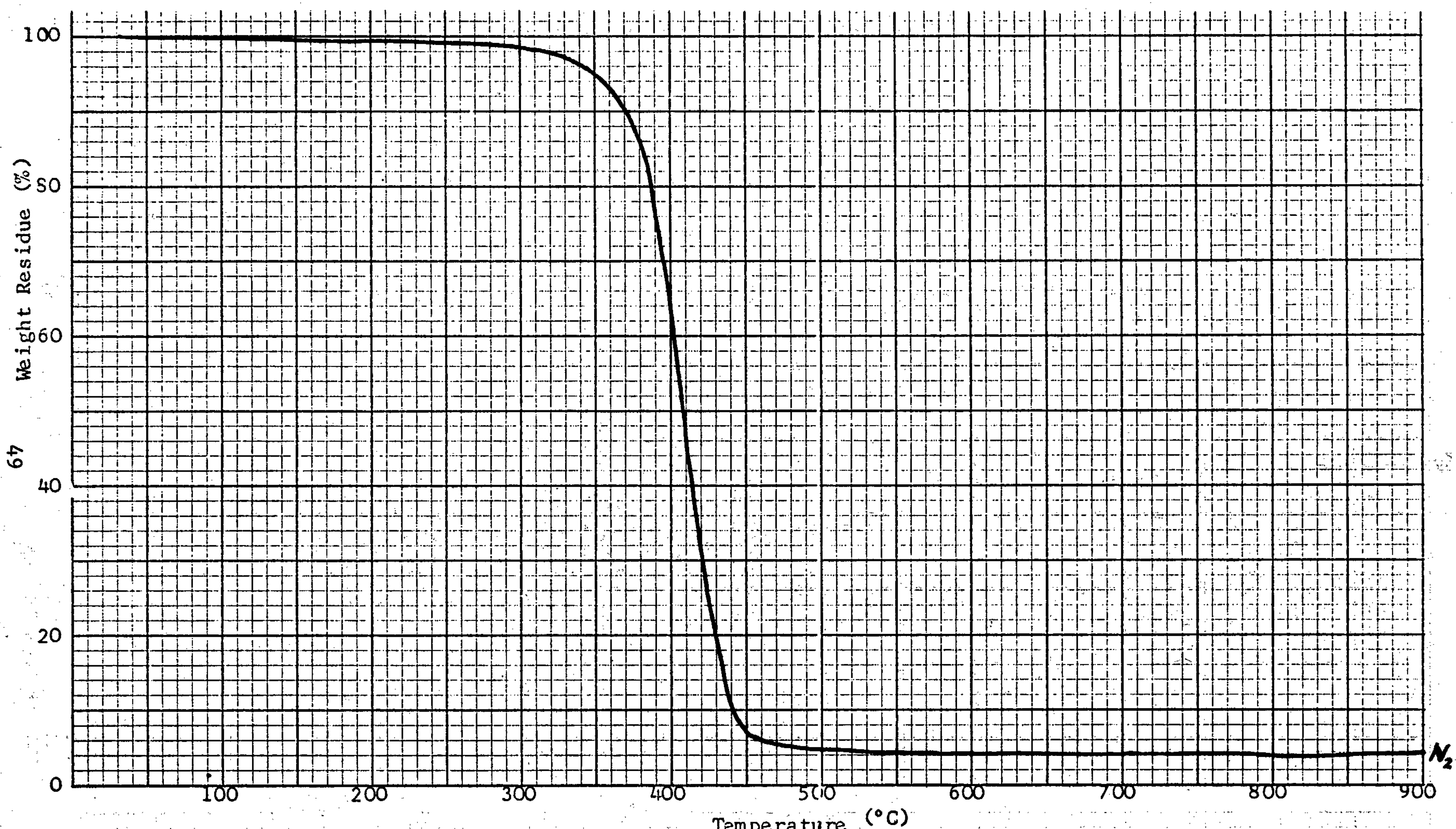



Fig. 4: TGA curve (nitrogen) of 6, 6 - Nylon.

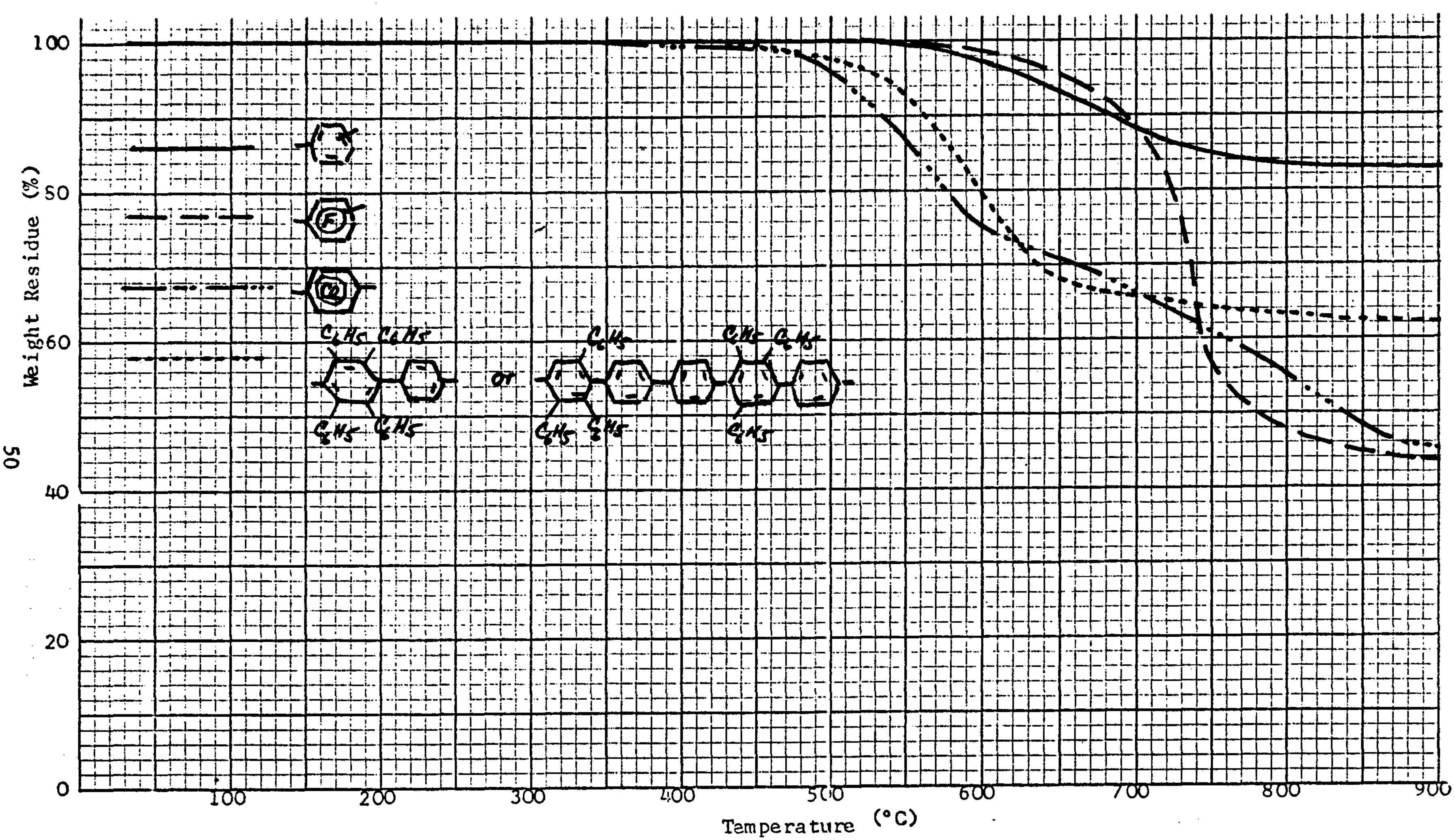



Fig. 5: Optimal TGA curves (nitrogen) of Polyphenylenes.

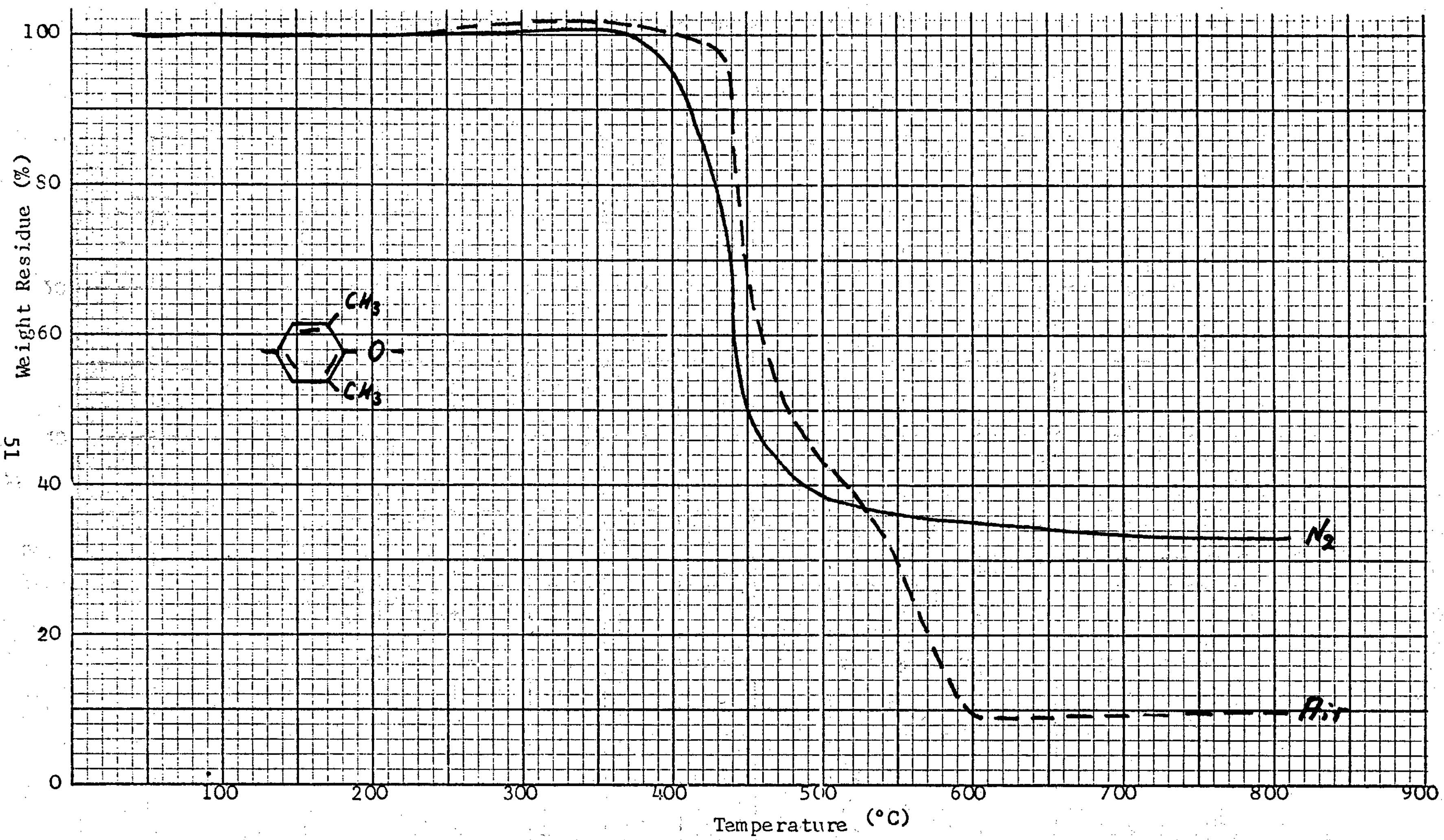



Fig. 6: TGA curves of Poly -2, 6- dimethylphenylene oxide.

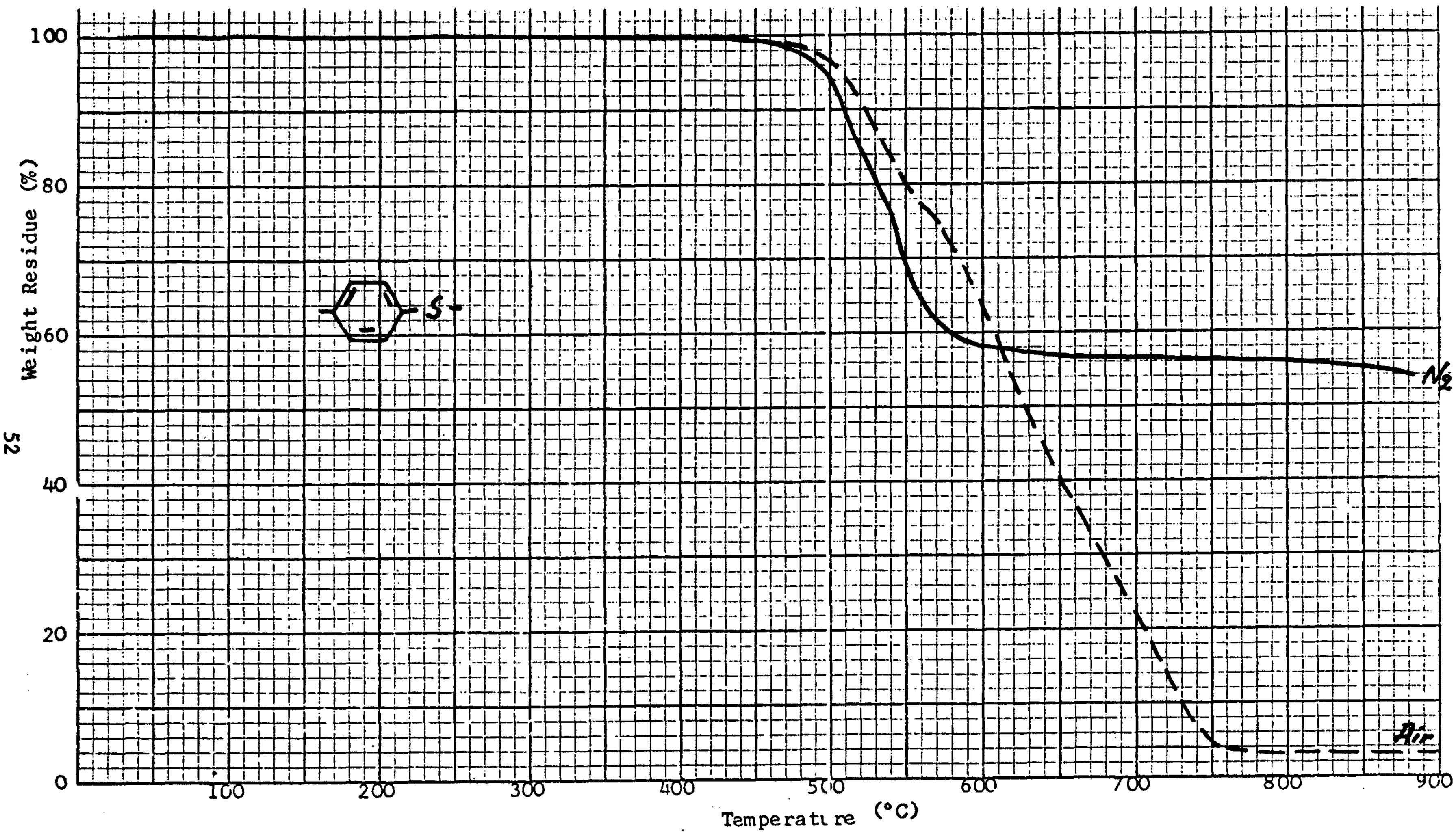



Fig. 7: TGA curves of Poly-p-phenylene sulfide.


Fig. 8: TGA curves of a Polyphexyleneether sulfone.

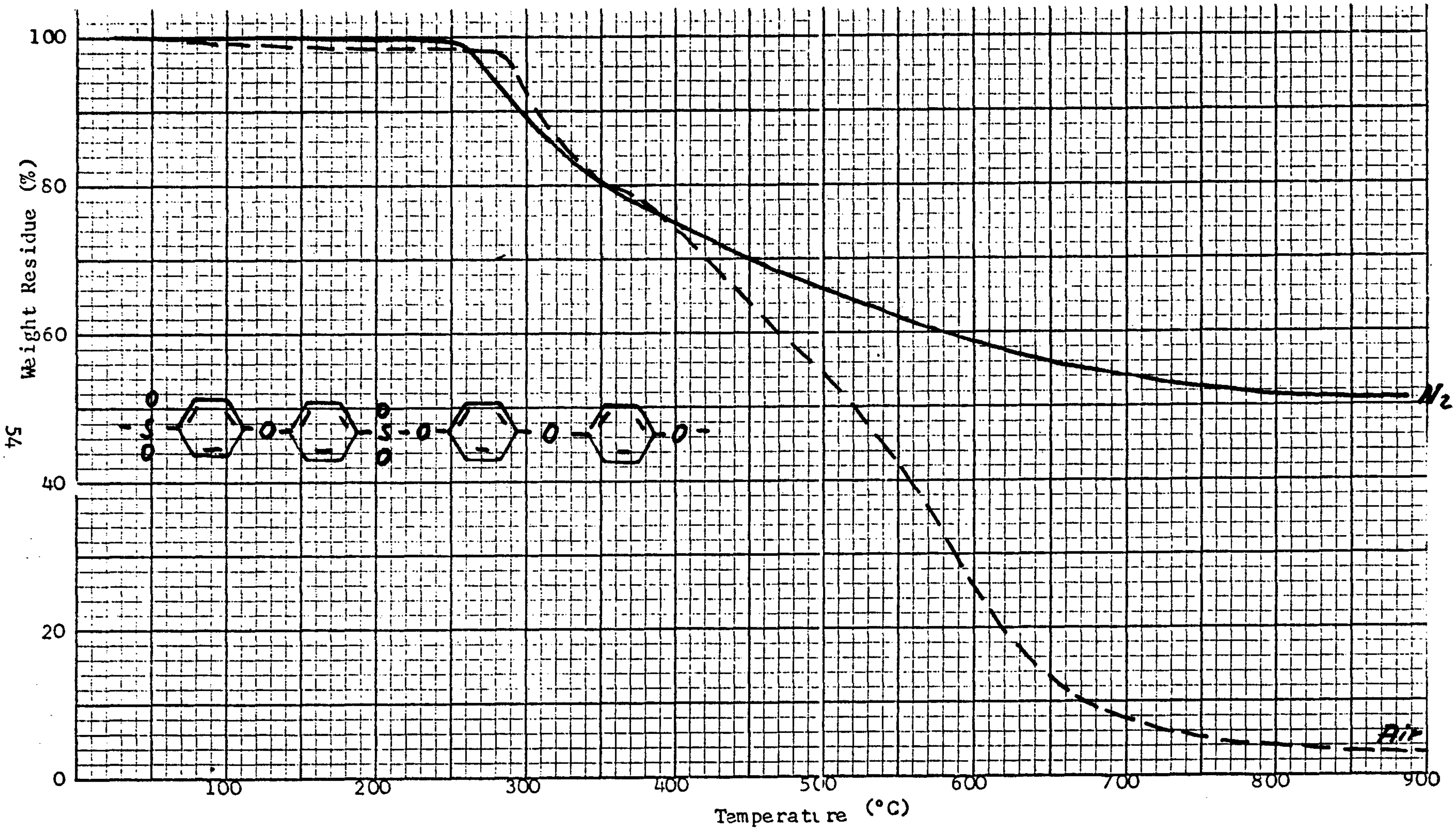



Fig. 9: TGA curves of a Polysulfonate.

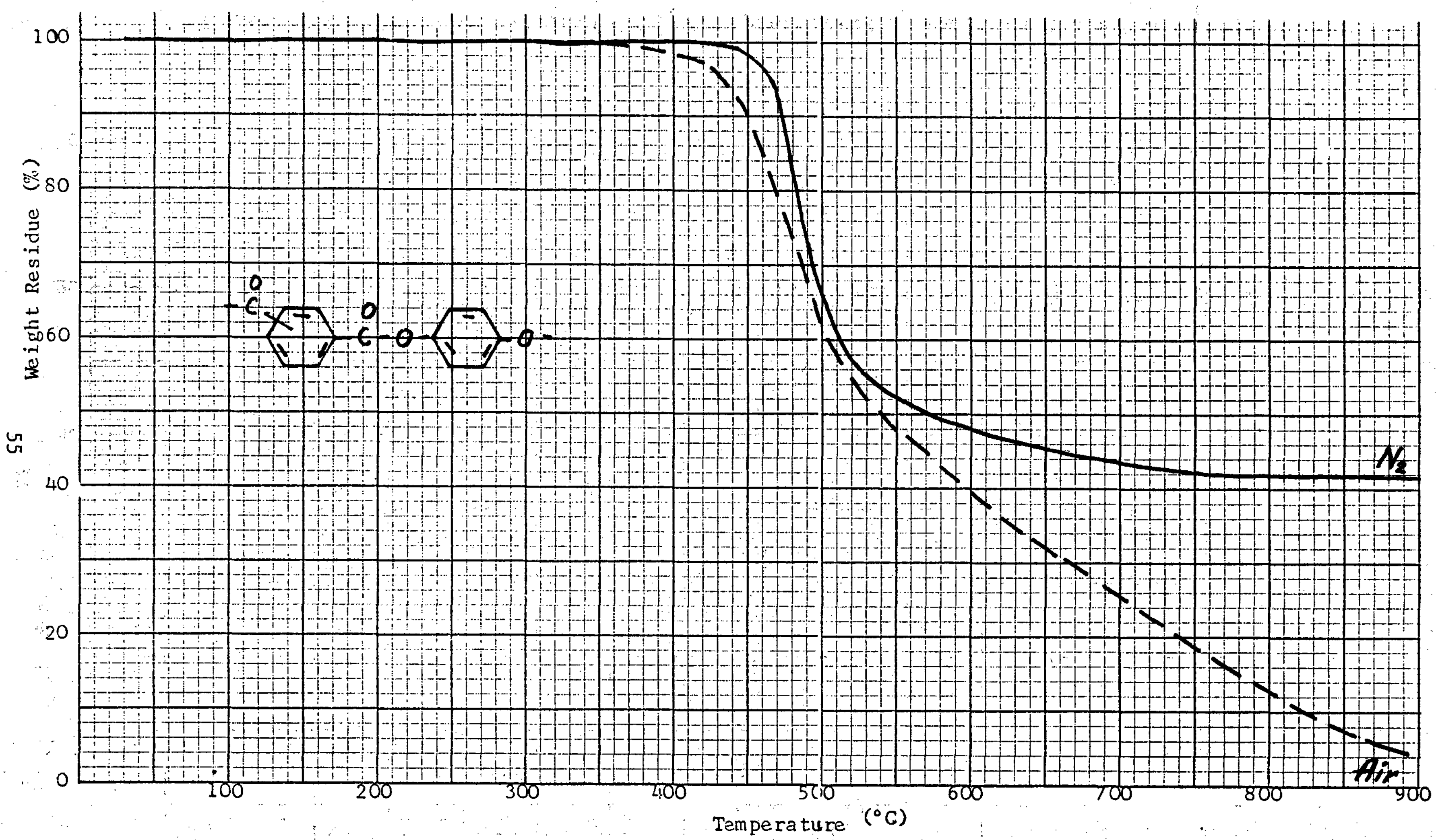



Fig. 10: TGA curves of an aromatic Polyester.

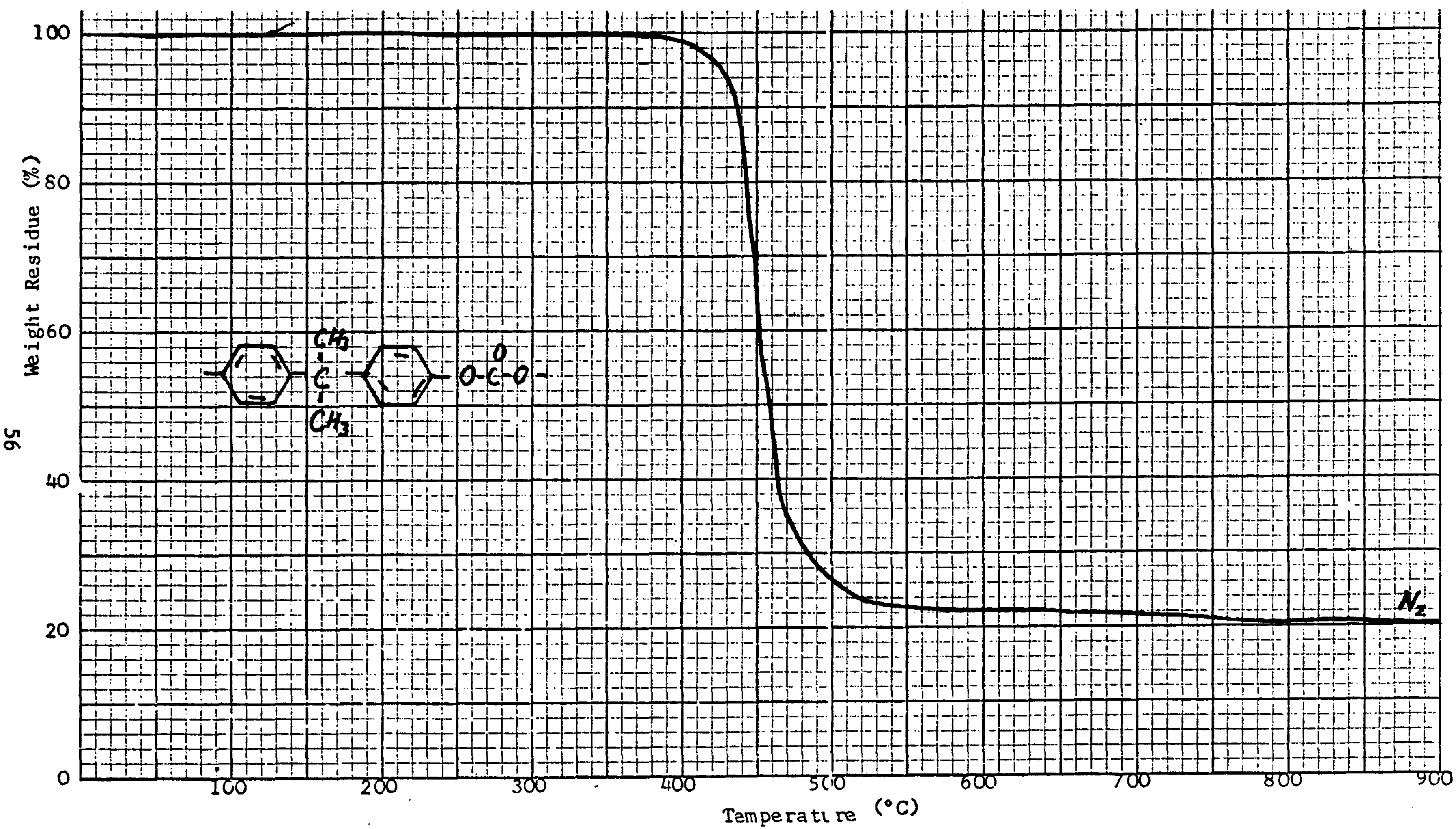



Fig. 11: TGA curve (nitrogen) of Poly[2,2-propane-bis (4-phenyl carbonate)].

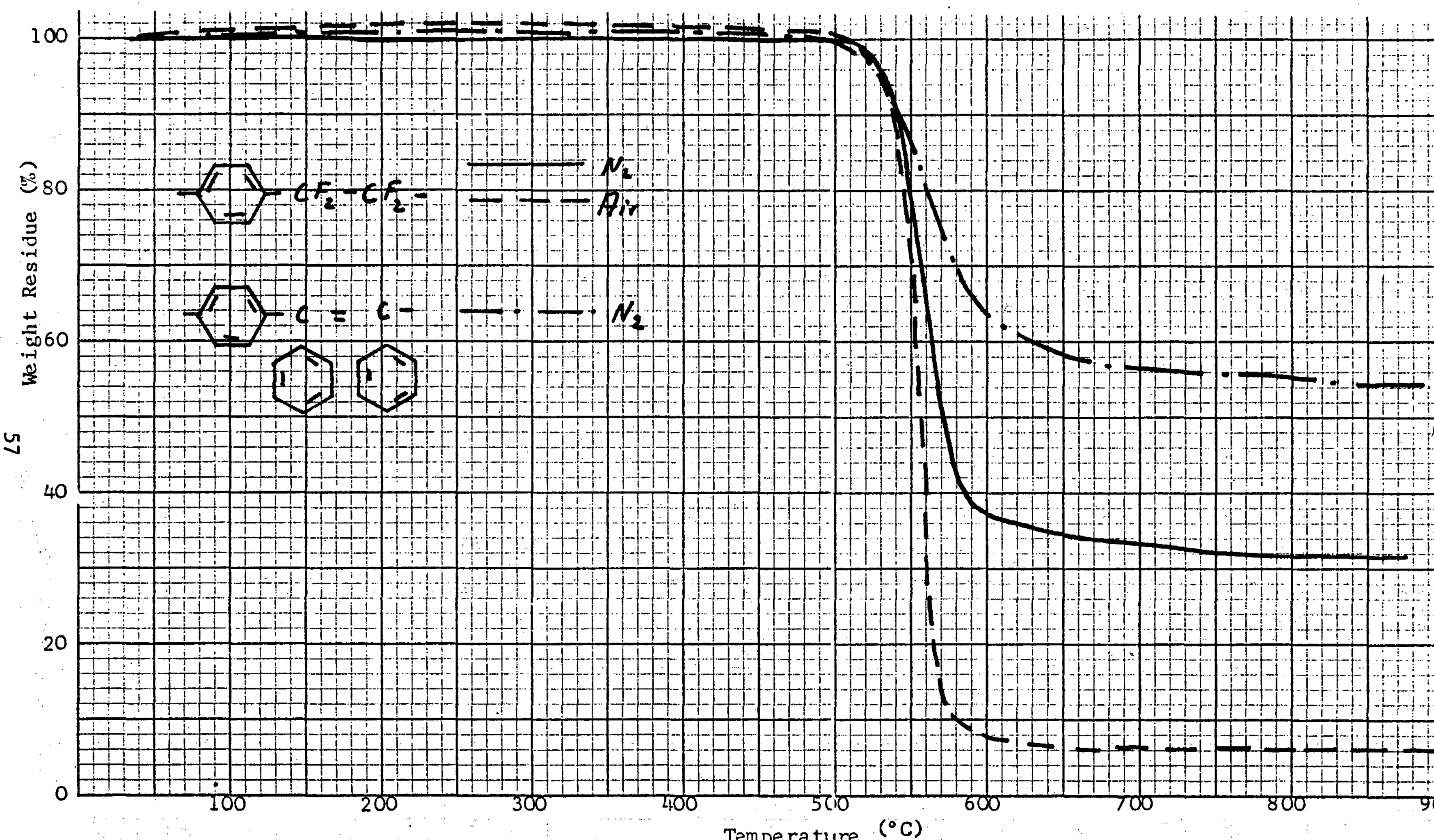



Fig. 12: TGA curves of a Polyxylylene and a Polyxylylidene.

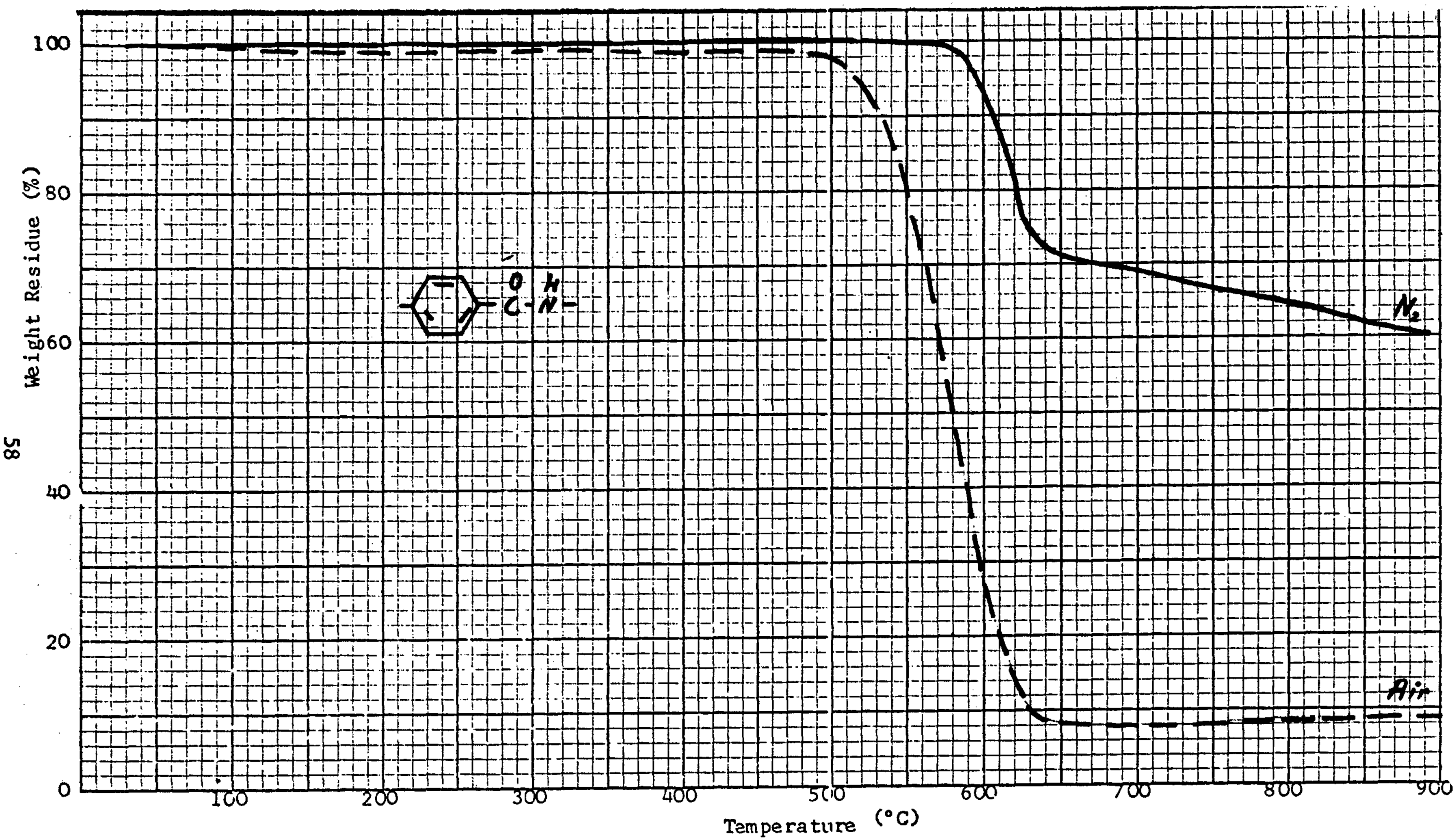



Fig. 13: TGA curves of a Polyamide.

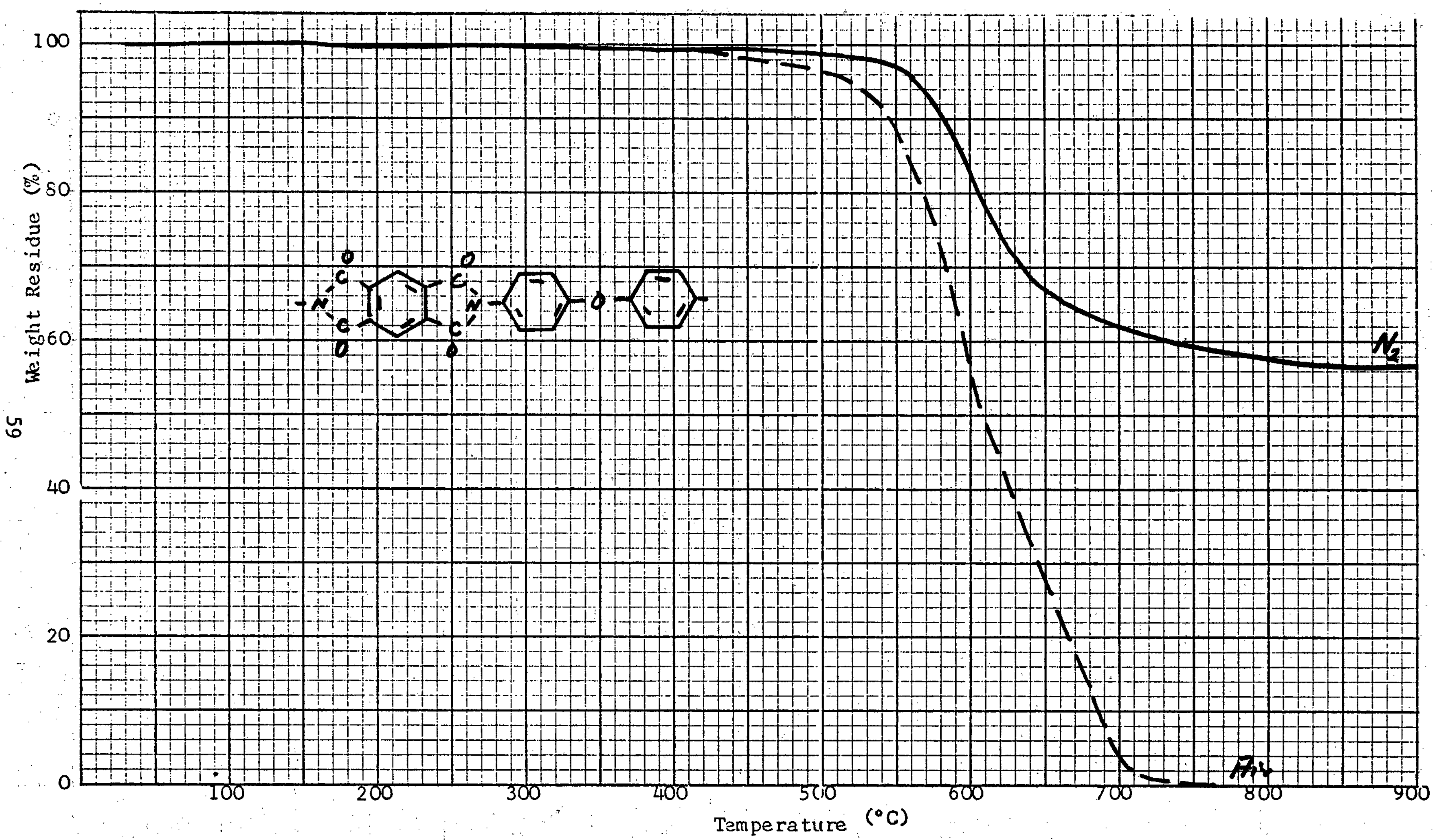



Fig. 14: TGA curves of a Polyimide.

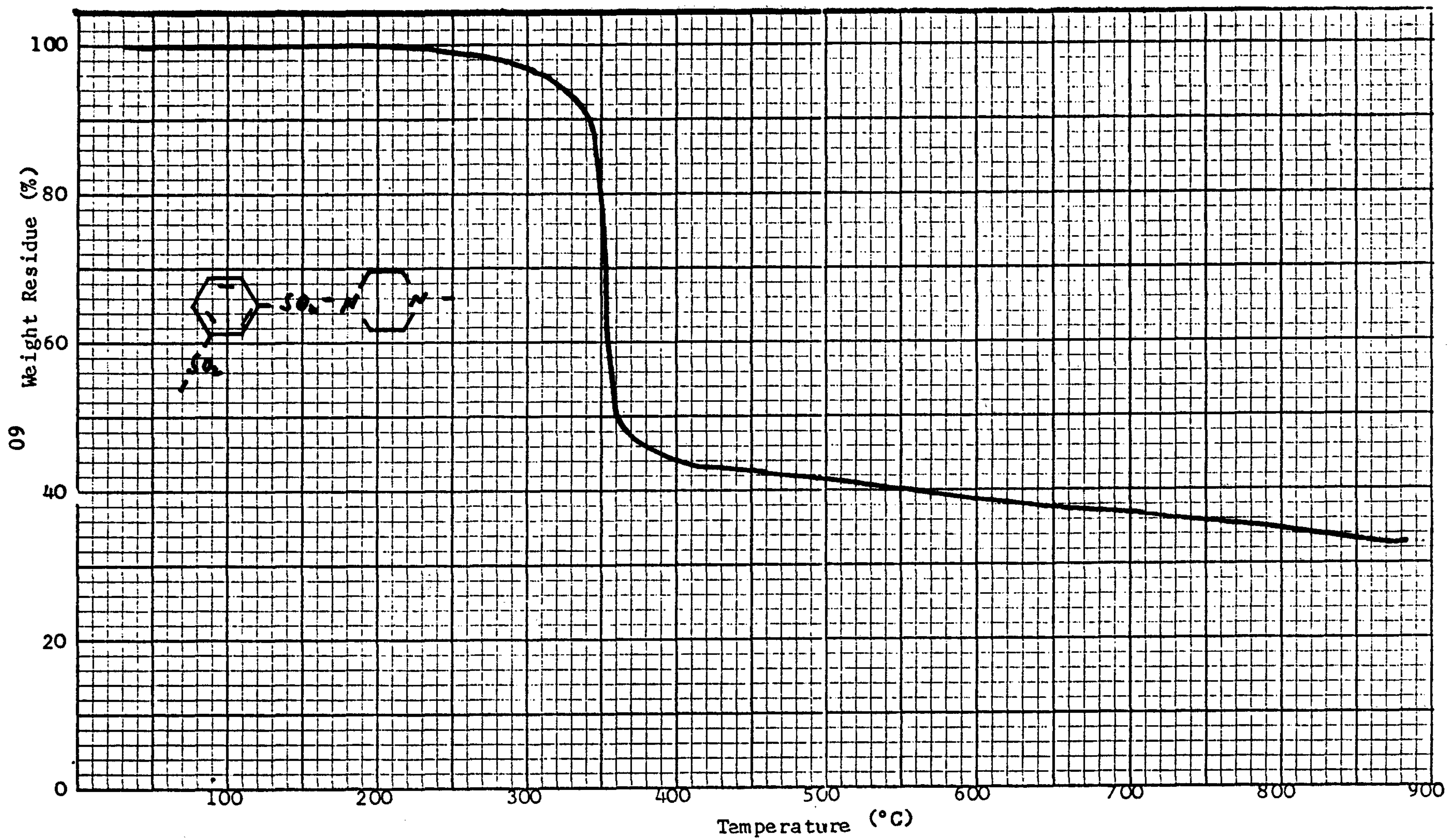



Fig. 15: TGA curve (nitrogen) of a Polysulfamide.

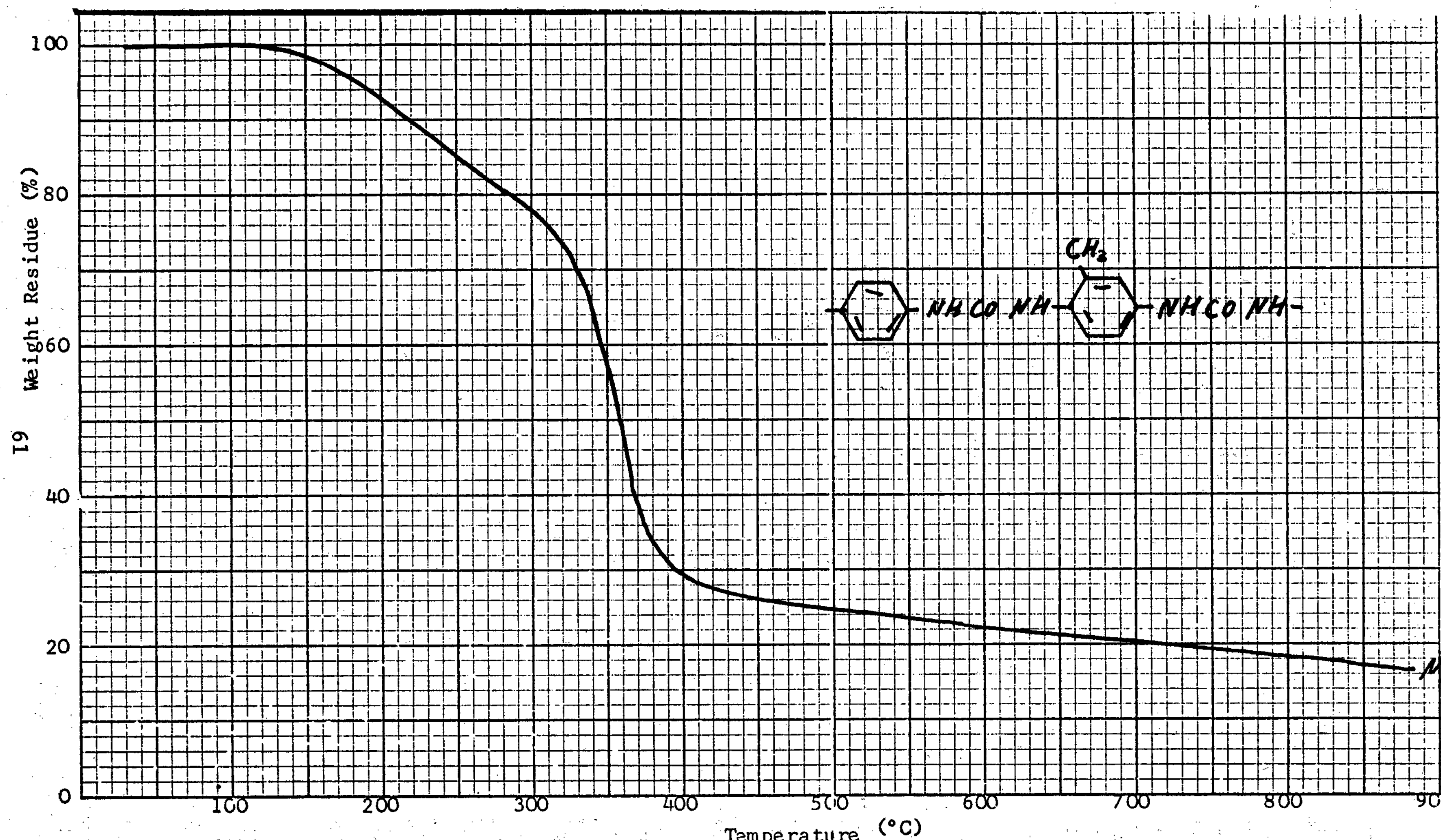



Fig. 16: TGA curve (nitrogen) of a Polyurea.

TABLE I:

Maximum Stabilities (Tdec's) of Polymer Repeat Units and Moieties in Nitrogen at $\Delta T$ = 3°C/min

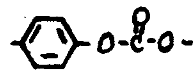
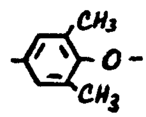
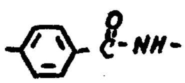
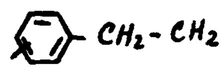
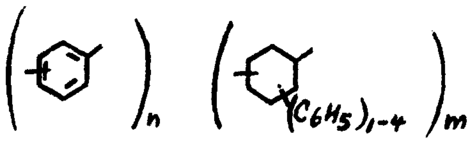
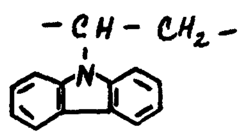
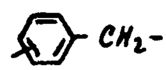
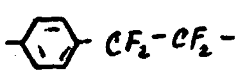
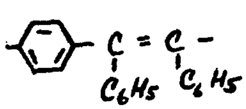
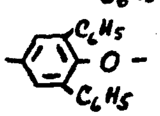
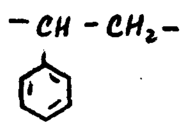
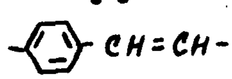
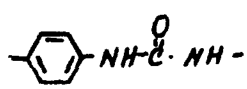
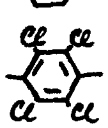
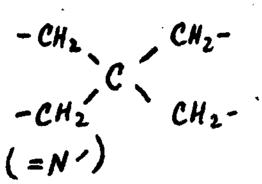
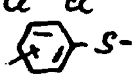
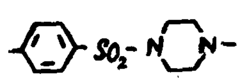
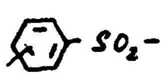
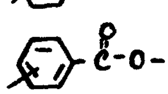
| | Tdec ($N_2$) | | Tdec ($N_2$) |
|---|---|---|---|
|  | 720 |  | 430 |
|  | 660 |  | 430 |
|  | 600 |  | 430 |
|  | 590 | $-CF_2-CFCl-$ | 420 |
| $-CF_2-CF-$ / $-CF_2-CF-$ | 585 | $-CH_2-CH_2-$ | 415 |
|  | 570 |  | 415 |
| $-CF_2-CF_2-$ | 540 |  | 410 |
|  (Phenol-Formaldehyde Resins) | 540 | $-CH_2-CH=CH-CH_2-$ | 390 |
|  | 535 | $-\overset{O}{\overset{\Vert}{C}}-NH-$ (aliph.) | 390 |
|  | 535 | $-O-CH_2-$ (epoxy) | 390 |
|  | 510 |  | 380 |
|  | 500 |  | 370 |
|  | 490 |  | 370 |
|  | 490 |  | 360 |
|  | 485 | $-O-\overset{O}{\overset{\Vert}{C}}-$ (aliph) | 340 |
|  | 480 | | |

TABLE I (cont.)

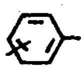
| | Tdec ($N_2$) |
|---|---|
|  $-SO_2-O-$ | 325 |
| $-CH_2-O-$ (in alicycl. sys.) | 320 |
| $-CF-CF_2-$  | 315 |
| $-NH-\overset{O}{\overset{\Vert}{C}}-O-$ (aliph.-arom.) | 310 |
| $-CH_2-O-$ | 290 |
| $-CH_2-SO_2-$ | 270 |
| $-CH_2-CHCl-$ | 260 |
|  $-N=N-$ | 240 |

TABLE II:

Approximate Order of Stabilities (Tdec($N_2$)) of Some Linking Units (R) between Phenylenes as Determined in Series of Aromatic Polymers

(Groups in order of decreasing stability; random listing within groups.)

1.) $-C(C_6H_5)_2-$ ; $-C(CF_3)(C_6H_5)-$ ; $-C(CF_3)_2-$ ;

$-CF_2-CF_2-$ ; $-C(C_6H_5)=C(C_6H_5)-$.

2.) $-CH=CH-$ ; $-CO-$ ; $-O-$ ; $-S-$ ; $-C(CH_3)(C_6H_5)-$ ;

$-CH(C_6H_5)-$ ; $-\overset{\overset{O}{\|}}{C}-NH-$.

3.) $-CH_2-$ ; $-C(CH_3)_2-$ ; $-SO_2-$

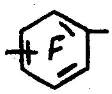
4.) $-C(CF_2Cl)_2-$ ; $-CH_2-CH_2-$ ; $-C(CH_3)_2-C(CH_3)_2-$ ;

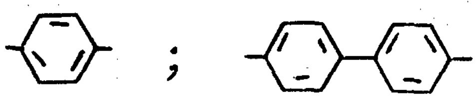
$-NH-$

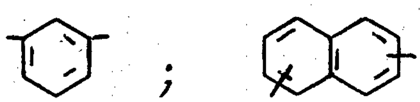
TABLE III:

Approximate Order of Stability (Tdec ($N_2$)) of Some Aromatic Units, as Determined in Series of Aromatic Polymers

(in order of decreasing stability)

1) 

2) 

3) 

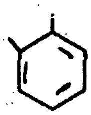
4) 

TABLE IV:

Average Relationship Tdec (air) versus Tdec (inert) *) for Polyaliphatics and Phenylene -R- Polymers

| Polymer Class | | | Tdec (air)/Tdec ($N_2$) (inert atoms) |
|---|---|---|---|
| I. | 2 | Fluorovinyl Polymers | 1.02 |
| | 10 | Spiro Polymers | 0.93 |
| | 11 | Polyphenylenes | 1.00 |
| | 13 | Polyphenylene oxides | 1.00 |
| | 14 | Polyphenylene sulfides | 1.01 |
| | 15 | Polyphenylene sulfones | 0.98 |
| | 17 | Aromatic Polyesters | 1.00 |
| | 19 | Polyxylylenes ($-CH_2-CH_2-$linkage) | 0.61 |
| | | ($-CF_2-CF_2$ linkage) | 0.96 |
| | 21 | Aromatic Polyamides | 1.00 |
| | 22 | Polyimides | 0.98 |
| | 23 | Polysulfamides | 0.97 |
| | 25 | Polymeric Schiff Bases | 1.00 |

*) refers to runs in nitrogen, helium or vacuum



*U.S.Government Printing Office: 1975 — 657-020/500